Sulfur Release during Alternative fuels Combustion in Cement Rotary Kilns

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Sulfur Release during Alternative Fuels Combustion in Cement Rotary Kilns

Maria del Mar Cortada Mut
Ph.D. Thesis
August, 2014
Preface

This dissertation summarizes the outcome of 3 years of research and is submitted partial fulfillment of the requirements for obtaining the Ph.D. degree at the Technical University of Denmark (DTU). The work has been carried out at the research center CHEC at the Department of Chemical and Biochemical Engineering at the Technical University of Denmark (DTU), in close collaboration with FLSmidth A/S. The project is part of the research platform “New Cement Production Technology”, financially supported by the Technical University of Denmark, FLSmidth A/S, and The Danish National Advanced Technology Foundation.

First of all, I would like to thank my supervisors Kim Dam-Johansen (DTU), Peter Glarborg (DTU) and Linda Kaare Nørskov (FLSmidth A/S) for their guidance and support during the supervision of this project. Thanks also to Anders Rooma Nielsen and Kim Hougaard Pedersen, who were involved in the supervision at some point during the 3 years. I would like to express my gratitude to all of them for their time, ideas, feedback, support, and fruitful discussions during the project.

Furthermore, I would like to thank current and former employees from DTU and FLSmidth that directly or indirectly have been involved in the project, especially thanks to Flemming Frandsen, Stig Wedel, and Ebbe Jøns for their help, patience, and knowledge sharing. Thanks to Erik Benzen for the collaboration and the great opportunity, and to his team for their assistance taking samples. Thanks to the PhD comics, which are always true in a cheer up way, and to the participants in 8th CemFuels conference for the big interest in my project, which gave me extra motivation to complete this project. Thanks to Søren Henkel and Tobias Hansen for their contribution to the project, to Nezam Azizaddini for the help with some figures, to the CHEC technicians group, the workshop at DTU and to the people at FLSmidth’s research center Dania and Valby, who have also been involved and helped in this project.

Finally, I would also like to thank to the Ph.D. students at CHEC, especially David Bogh, Claus Maarup, and Thomas Klint, for providing a pleasant working atmosphere, and of course for enjoyable lunches, fruitful discussions, and the social activities we have had.

At last but not least, thanks to my family and friends for all their support through the last 3 years, "Moltes Gràcies!" and big thanks to Per, who has been there in all moments.

Maria del Mar Cortada Mut

Kgs. Lyngby, August 2014.
Abstract

Cement production is an energy-intensive process, which has traditionally been dependent on fossil fuels. However, the usage of selected waste, biomass, and by-products with recoverable calorific value has increased due to the lack of experience in handling the different and varying combustion characteristics caused by different chemical and physical properties, e.g. higher moisture content and larger particle sizes.

When full combustion of alternative fuels in the calciner and/or main burner is not achieved, partially or unburned solid fuels may drop into the material bed in direct contact with the bed material of the rotary kiln. The combustion of alternative fuels in direct contact with the bed material of the rotary kiln causes local reducing conditions and may alter the input and the behavior of minor elements into the kiln system.

The minor elements of concern are sulfur, chlorine, sodium, and potassium, which are known to be circulating or volatile elements in the kiln system. Compounds containing these elements evaporate when exposed to high temperatures, and may subsequently condense in cooler parts of the plant. High internal circulation seriously affects the process stability and operation of the cement kiln system, such as material build-ups in the cyclones and/or in the rotary kiln as rings, and on a longer time-scale by shell corrosion.

This thesis provides a detailed analysis of the circulation of the volatile elements and the transformation of different species containing these elements at different locations in the cement plant. This is complemented by thermodynamic calculations for a better understanding of the inorganic chemistry in the rotary kiln. The main focus is given to SO$_2$ release due to decomposition of calcium sulfate in the kiln inlet and the modification of the sulfur circulation during alternative fuel combustion, because sulfur is the most affected element by reducing combustion conditions.

Sulfur release from cement raw materials during alternative fuel combustion is experimentally investigated using pine wood and tire rubber particles in a pilot scale set-up, which is able to simulate the process conditions in the material inlet end of an industrial rotary kiln. The SO$_2$ release increases with decreasing fuel particle size, oxygen content in the freeboard gas, and increasing sulfur content in the bed material. Experiments with wood with different degree of volatiles show that the sulfur release mainly takes place during devolatilization. This is supported by the finding of the industrial investigation on sulfur released, where no clear relationship is observed between the carbon from the fuel, mainly expected to be in the form of char, entering in the rotary kiln and the sulfur recirculation.

The effect of different concentrations and binary mixtures of the main reducing agents released from fuels on sulfur release are investigated experimentally in order to separate the influence of the simultaneous phenomena occurring in the experimental set-up, such as mixing the fuel with the bed material, heating up of a particle, and on a longer time-scale by shell corrosion.

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devolatilization, char combustion, the reactions between CaSO₄ and the different reducing agents, and the oxidation of the volatiles gases in the freeboard. The main reducing agents are CO, CH₄, and H₂, which are introduced under the bed material in the high temperature rotary drum to characterize the SO₂ release under variation of temperature, oxygen content in the gas, and time of exposure. A threshold concentration for each reducing gas, below which no SO₂ release occurs, is found. The reducing concentration and the time of exposure are of high importance for SO₂ release because it is shown that introducing the same total amount of gas, the highest reducing agent concentration for a short period released a higher total SO₂ amount compared to the lowest concentration during a long period.

A mathematical reaction based model for predicting sulfur release caused by volatiles from wood particles fired in the material kiln inlet is developed and evaluated against pilot scale data, which shows that the model follows the experimental data tendency. The model can predict SO₂ release varying particle size, fill degree, and firing degree but the effect of sulfur content in the bed cannot be predicted. Further development regarding particle motion according to the rotational speed may be needed. Furthermore, a model for predicting the tendency of build-ups for a kiln system is developed based on the prediction of SO₃ and Cl concentrations in the hot meal. The predictions can be performed for a kiln system operating only with fuel in the calciner and kiln burner, and the influence of bypass operation can be added as well as alternative fuels substitution in the kiln inlet.

The sulfur release in the inlet of the rotary kiln can be minimized if the fuel combustion takes place at temperatures lower than 800 °C and can be avoided when the volatile gases from fuels are not released in contact with the bed material.
Afhandlingen fokuserer på SO₂frigivelse på grund af nedbrydning af cementråmaterialer under forbrænding og forbrænding af alternative brændsler, fordi svovl er det mest påvirkede element under reducerende forbrændingsbetingelser.

Svovlfrigivelse fra cementråmaterialer under forbrænding af alternative brændsler, repræsenteret af fyrretræ og gummipartikler af dæk, er undersøgt eksperimentelt i en pilotskala opstilling, som er i stand til at simulere procesbetingelserne i materieindløbet af en industriel roterovn. SV: frigivelsen stiger med faldende brandeselpartikelstørrelse, ilindhold i atmosfæren og stigende indhold af svovl i fyldningsmaterialet. Forsøg med træ med forskellig indhold af flygtige stoffer viste, at frigivelsen af svovl hovedsageligt fandt sted under afgasningen. Dette er i god overensstemmelse med resultaterne af den industrielle undersøgelse om frigivelse af svovl udført i dette projekt, hvor ingen direkte sammenhæng mellem kulstof fra brandesel, hovedsageligt forventet at være i form af koks, som ender i ovnindløbet og svovlcirkulationen kunne påvises.

Virkningen af forskellige koncentrationer af de vigtigste reduktionsmidler og binære blandinger heraf som frigøres fra brændstoffer er undersøgt eksperimentelt for at adskille indflydelsen af de samtidige fenomener i den eksperimentelle opsætning, såsom opblanding af brændstoffet med fyldningsmaterialet,
partikelopvarmning, pyrolyse, koksforbrænding, reaktionerne mellem CaSO₄ og de forskellige reduktionsmidler, og oxidation af flygtige gasser i gasfasen. De vigtigste reduktionsmidler er CO, CH₄ og H₂, som blev indført under fyldningsmaterialet i en roterende højtemperaturtromle for at karakterisere SO₂ frigivelse under varierende temperaturer, ilinthold og eksponeringstid. En grænseværdi for koncentrationen af hver reducerende gas, hvorunder der ikke forekommer SO₂ frigivelse, blev fundet. Koncentration af den reducerende specie og eksponeringstiden er af stor betydning for den totale SO₂ frigivelse, fordi det blev påvist ved indførelse af den samme samlede mængde gas, at en høj reducerende koncentration i løbet af en kort periode medførte en højere samlet SO₂ frigivelse i forhold til en lav koncentration i en længere periode.

En matematisk reaktionsbaseret modell kan forudsige SO₂ frigivelse for varierende partikelstørrelse, fyldningsgrad og fyringsgrad, med effekten af svovlindholdet i fyldningen kan ikke forudsiges. Yderligere udvikling vedrørende partikelbevægelse som funktion af rotationshastigheden kan være nødvendig. Henudover er der et model til forudsigelse af materialibygningstendens for en ovn blevet udviklet, baseret på forudsigelse af SO₂ og Cl koncentrationer i ovnindløbsmaterialet. Forudsigelserne kan udføres for et ovnsystem med brændselstilknytning kun i kalkinatoren og roterovensbænderen, og derudover kan indflydelsen af bypaas og alternative brændstoffer tilføjes.

Svovlfrigivelsen i ovnindløbet af roterovnen kan minimeres, hvis forbrændingen sker ved temperaturer lavere end 800 °C, og kan udfølges hvis afgasningen af de flygtige forbindelser fra brændselne ikke sker i direkte kontakt med fyldningsmaterialet.
Table of Contents

1. Introduction ........................................................................................................... 1
   1.1 Background ........................................................................................................ 1
   1.2 Project Objectives ............................................................................................ 2
   1.3 Structure of the Ph.D. Thesis ............................................................................. 2
   1.4 References ........................................................................................................ 3

2. Cement Chemistry and Production ........................................................................... 5
   2.1 Introduction ........................................................................................................ 5
   2.2 Cement Chemistry .............................................................................................. 6
   2.2.1 Raw Materials ............................................................................................... 6
   2.2.2 Calcination .................................................................................................... 6
   2.2.3 Clinker Reactions .......................................................................................... 7
   2.3 Cement Production ............................................................................................. 8
   2.3.1 Preparation of Raw Materials ....................................................................... 9
   2.3.2 Pyro Processing ............................................................................................. 10
   2.3.3 Clinker Processing ....................................................................................... 12
   2.3.4 Process Data Overview ................................................................................. 12
   2.4 Conclusions ....................................................................................................... 13
   2.5 References ....................................................................................................... 13

3. Alternatives Fuels in the Cement Production ............................................................ 17
   3.1 Introduction ....................................................................................................... 17
   3.2 Combustion of Alternative Fuels ...................................................................... 21
   3.2.1 Combustion Studies of Alternative Fuels .................................................... 24
   3.2.2 Volatile Gases from Fuels ........................................................................... 25
   3.3 Technologies for Alternative Fuels Combustion ............................................. 28
   3.3.1 External reactors ............................................................................................ 29
   3.3.2 Kiln burners .................................................................................................. 30
   3.3.3 Emerging technologies .................................................................................. 31
   3.4 Conclusions ...................................................................................................... 32
   3.5 References ...................................................................................................... 33

4. Circulation of Inorganic Elements in the Kiln System ................................................. 39
   4.1 Circulation of Volatiles Elements ..................................................................... 39
   4.1.1 Reaction Affinity between Volatile Elements ............................................ 40

References ..................................................................................................................... 33

Conclusions .................................................................................................................... 12

Emerging technologies ....................................................................................................
External reactors ............................................................................................................
Volatile Gases from Fuels .............................................................................................
Clinker Processing ........................................................................................................
Process Data Overview ..............................................................................................
Conclusions ..................................................................................................................
6. Effect of Different Pyrolyzed Gases on Sulfur Release

6.1 Literature Study of the CaSO\textsubscript{4} Reductive Decomposition

6.1.1 Carbon Monoxide

6.1.2 Hydrogen

6.1.3 Methane

6.1.4 Alternating Oxidizing and Reducing conditions

6.1.5 Pre-experimental Considerations

6.2 Experimental

6.3 Results and Discussion

6.3.1 Carbon Monoxide

6.3.2 Methane

6.3.3 Hydrogen

6.3.4 Carbon Monoxide, Hydrogen, and Methane Comparison

6.3.5 Binary Mixtures

6.3.6 Thermal Decomposition of CaSO\textsubscript{4}

6.4 Conclusions

6.5 References

7. Modeling the Sulfur Release in the Inlet of the Rotary Kiln

7.1 Literature Study on Rotary Kilns Models for the Cement Industry

7.1.1 Review of Rotary Kiln Models

7.1.2 Kiln System Models including Alternative Fuels Usage

7.2 System Description and Modeling approach

7.3 Assumptions

7.4 Mathematical Development

7.4.1 Calculation of the Particle Temperature Profile

7.4.2 Calculation of Pyrolysis

7.4.3 Rotary Kiln Model

7.5 Results

7.5.1 Substitution 10 % Energy with Alternative Fuels fired in the Kiln Inlet

7.5.2 Effect of Firing Degree in the Kiln Inlet

7.5.3 Sensitivity analysis

7.6 Model Validation

7.7 Conclusions

7.8 References
1. Introduction

1.1 Background

Cement production is an energy-intensive process, which requires approximately 3 MJ/kg cement clinker produced, equivalent to 60-130 kg coal/ton of cement clinker depending on the type of coal (VDZ, 2009). The energy consumed by the cement industry is estimated to constitute about 2% of the global primary energy consumption (Rubenstein, 2010; Worrell et al., 2001).

During the last decades, an interest in replacing fossil fuels with selected waste, biomass, and by-products with recoverable calorific value, defined as alternative fuels, has arisen in order to minimize production cost and due to environmental concerns (Lechtenberg and Diller, 2012). The introduction of alternative fuels is however not straightforward because it may influence emissions, product quality, process efficiency, and process stability of the cement production plant.

Furthermore, alternative fuels may be partly or fully CO$_2$-neutral, which may be important from an environmental point of view. The European cement industry recovers a substantial amount of waste-derived fuels, which replace fossil fuels up to a level of more than 80% in some individual plants (European IPPC, 2013). The change in energy sources is illustrated in Figure 1-1 and Figure 1-2, which show the type of the fuels used in average by the cement industry in Europe in 1990 and 2011, respectively.

In comparison with fossil fuels, alternative fuels typically consist of relatively large particles, which are difficult to downsize, and may have different chemical and physical properties. This will be elaborated in Chapter 3. Despite these differences, alternative fuels are fired at the traditional firing points of a cement plant (calciner and kiln burner) or directly in the rotary kiln. The combustion of alternative fuels at these location may have some consequences (Nielsen, 2011), which are:
The main technical subject of this Ph.D. project has been to investigate the consequences of the combustion of solid alternative fuels in cement production. The project has focused on the sulfur release from the bed material close to the inlet of the rotary kiln. The strategy is first to provide a detailed analysis of the inorganic chemistry in the kiln system and how it may be affected by utilization of alternative fuels in the material inlet end. Experiments with solid fuels and reducing gases have been conducted in a pilot-scale rotary drum in order to understand the behavior of the sulfur release at the inlet of the rotary kiln. The experimental data were also used for the validation of a mathematical model capable of qualitatively predicting the SO₂ release from the bed material. The tendency of build-ups when using alternative fuels can be predicted on basis of the model and consequently operational problems may be avoided.

The knowledge obtained may be used to improve the design basis of cement plants, redesign of existing technology or to develop new technology in order to minimize the sulfur release, and operational problems such as build-ups, due to the combustion of solid alternative fuels in the calciner and/or in the inlet of the rotary kiln.

1.3 Structure of the Ph.D. Thesis

Chapter 2 provides an introduction to the cement chemistry and production. Chapter 3 introduces the general characteristics of alternative fuels in cement production and reviews the current status regarding combustion of solid alternative fuels and the available technologies. The inorganic chemistry consisting of the volatile elements (S, Cl, K, and Na) in the kiln system is described in details in Chapter 4. The consequences related to the combustion of alternative fuels are also reviewed; special attention is given to the modification of the sulfur circulation. Furthermore, the inorganic chemistry along the rotary kiln is studied by thermodynamic equilibrium calculations.
Chapter 5 describes the experiments with sulfur release from raw materials during solid fuel combustion, focusing on fuel particle size, degree of fuel devolatilization, and moisture content. Experiments quantifying the sulfur release from raw materials by introduction of CO, CH₄, and H₂, and their mixtures under the bed material are explained in Chapter 6. Chapter 7 contains the development of a mathematical model for predicting sulfur release in the inlet of the rotary kiln. The results are further used to predict the tendency of build-ups, which is described in Chapter 8. An analysis of industrial experience with focus on sulfur release is provided in Chapter 9. The chapter determines the calciner fuel conversion, the tendency of build-ups and the sulfur volatility. An analysis of the current challenges with monitoring and controlling sulfur release in the cement plants is also provided. Finally, the overall conclusions regarding the sulfur release during combustion of alternative fuels in the rotary kiln material inlet end and suggestions for further work are provided in Chapter 10.

1.4 References


2. Cement Chemistry and Production

This chapter seeks to provide a fundamental understanding of the cement chemistry and the cement production, which is necessary for the understanding of the subsequent chapters.

2.1 Introduction

Cement has been known as a binder material since ancient times, but the manufacturing process has evolved greatly since then. Nowadays, cement is one of the most important materials, used for production of concrete and mortar in the construction sector. Cement and mortar are used for bonding of natural and artificial aggregates in infrastructure and in many building materials (Cembureau, 2009). The most commonly used type of cement is the so-called Portland cement. Several other types of cement with other characteristics are also produced for specific purposes. However, this thesis will focus on the Portland cement.

The industrial production of cement started in the middle of the 19th century with the development of the continuous kiln. One of the first continuous kilns was the shaft kiln, which bears a high degree of resemblance to a blast furnace. In the end of the 19th century, the shaft kiln was replaced by the rotary kiln, which is still an important part of a modern cement plant (Schneider et al., 2011).

Cement production is a very energy-consuming process. The energy costs account typically for 30-40% of the total costs of the cement production. Cement production is an industrial sector that has been growing steadily since the end of World War II. The annual global cement production grew from 100 million tons in 1950 (van Oss, 2005), to 2600 million tons in 2006 (U.S. Geological Survey, 2007). After a decrease in production due to the global economic down of 2007-2009, the cement production has recovered and in 2013 a total of 4 billion tons cement was estimated to be manufactured worldwide (U.S. Geological Survey, 2014). The cement industry accounts for around 5% of the global CO2 emissions (World Energy Council, 2008), making it one of the more greenhouse emissions-intense industries.

2.2 Cement Chemistry

Portland cement is a hydraulic binder that sets and hardens by hydration (Hewlett, 1998) and is manufactured from Portland cement clinker, which consists of a mixture of burned limestone, sand, and clay. The clinker is ground and mixed with gypsum (calcium sulfates) and other minerals may be added to obtain cement with the desired performance in terms of setting time and strength development (Cochez and Wouter, 2010).

Portland clinker consists mainly of belite, alite, ferrite and aluminate, comprising more than 90 wt. % of the product. The typical content of these minerals are displayed in Table 2-1. Subsequently, 3-6 wt. % of gypsum is added to the clinker and the mixture is finely ground to form the finished cement (Theisen, 2007).
Calcination is the first major chemical change in the thermal treatment of the raw materials and consists of the thermal decomposition of calcium carbonate into calcium oxide and carbon dioxide as shown in reaction (2-1). The calcination occurs in the temperature range of 700-900 °C.

\[ \text{CaCO}_3(s) \rightarrow \text{CO}_2(g) + \text{CaO}(s) \quad \Delta H = -1782 \text{ kJ/kg CaCO}_3 \]  

Table 2-1: Main constituents of Portland cement clinker (Hewlett, 1998; Taylor, 1997).

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical composition</th>
<th>Nomenclature</th>
<th>Approximate content [wt. %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Belite</td>
<td>(CaO):SiO$_2$</td>
<td>C:S</td>
<td>15-30</td>
</tr>
<tr>
<td>Alite</td>
<td>(CaO):SiO$_2$</td>
<td>C:S</td>
<td>50-70</td>
</tr>
<tr>
<td>Ferrite</td>
<td>(CaO):Al$_2$O$_3$-FeO</td>
<td>C:AF</td>
<td>5-10</td>
</tr>
<tr>
<td>Aluminate</td>
<td>(CaO):Al$_2$O$_5$</td>
<td>C:A</td>
<td>5-15</td>
</tr>
</tbody>
</table>

The major mineral phase in the Portland cement is tricalciumsilicate, often referred to as alite. Alite is responsible for setting and development of early strength, because it is relatively fast reacting. Dicalcium silicate, belite, controls the late strength due to its slow reactivity properties. Ferrite and aluminate are present due to the need to obtain a liquid at the peak kiln temperature (1400-1450 °C), facilitating the formation of the desired silicate phases during the clinker reactions. Besides these phases, cement contains from 0.5 to 1.5 % of free lime (CaO), and 1 % of SO$_3$, and a small proportion of MgO. Clinker has typically a mass content of 67 % CaO, 22 % SiO$_2$, 5 % Al$_2$O$_3$, 3 % Fe$_2$O$_3$, and 3 % other components (Taylor, 1997).

2.2.1 Raw Materials

The typical mixture of raw materials used for Portland cement contains ground limestone, clay, shale, and sand, introducing the various elements needed for clinker formation. Calcium is mainly provided by raw materials such as limestone, marl, or chalk and constitutes approximately 75-80 wt. % of the raw materials. Silica, aluminum, and iron components, as well as other elements, are provided by clay, shale, and other materials. Small amounts of additives such as iron ore, bauxite, and shale may be needed to provide additional iron oxide (Fe$_2$O$_3$), alumina (Al$_2$O$_3$) and silica (SiO$_2$) to adjust the chemical composition of the raw mix to the process and product requirements (Hewlett, 1998; Bye, 1999). The different kinds of raw materials needed to achieve the required cement composition are ground and mixed to produce a homogeneous blend, which is processed in the kiln (CSI, 2005).

Selected waste and by-products, such as blast furnace slag and fly ash, containing useful minerals are also used in the production of cement. The usage of waste as a replacement for conventional raw materials decreases the demands on local landfills. Hence, the overall environmental impact is reduced (CSI, 2005).

2.2.2 Calcination

Calcination is the first major chemical change in the thermal treatment of the raw materials and consists of the thermal decomposition of calcium carbonate into calcium oxide and carbon dioxide as shown in reaction (2-1). The calcination occurs in the temperature range of 700-900 °C.

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The reaction is highly endothermic and consumes around 60% of the total energy required for the production of cement (Hewlett, 1998). The energy required by the calcination process comes from the combustion of fuels in the calciner, which is the furnace where calcination takes place (see Figure 2-2 and Figure 2-3). The degree of calcination, which is the degree of dissociation of the calcium carbonate, is typically around 90-95% in a modern calciner kiln system (Taylor, 1997).

### 2.2.3 Clinker Reactions

Clinker reactions occur at temperatures between 700 and 1450 °C. The reactions may be affected by minor compounds and involve intermediate compounds before the formation of the final clinker product. A general description of the overall clinker reactions are presented in reactions (2-2) to (2-5). A detailed overview of the chemistry, phase relations, etc. is provided elsewhere (Hewlett, 1998; Bye, 1999).

The formation of belite from lime and silica, reaction (2-2), starts at temperatures above 700 °C.

\[
2\text{CaO}(s) + \text{SiO}_2(s) \rightarrow (\text{CaO})_2 \cdot \text{SiO}_2(s) \quad (2-2)
\]

Above 1300 °C, the proportion of clinker liquid increases and nodules are formed. At the same time, intermediate phases dissociate to form liquid and belite. The belite reacts with free lime to form alite, according to reaction (2-3). A clinker temperature of about 1450 °C is required in order to obtain a proper product quality. A proper clinker quality has an alite content of minimum 50 wt. % and a free lime content of maximum of 1.5 wt. % (Taylor, 1997).

\[
\text{CaO}(s) + (\text{CaO})_2 \cdot \text{SiO}_2(s) \rightarrow (\text{CaO})_3 \cdot \text{SiO}_2(s) \quad (2-3)
\]

The formation of solid aluminate and ferrite from the liquid phase takes place when the temperature drops to 1250 °C, according to reactions (2-4) and (2-5).

\[
3\text{CaO}(s) + \text{Al}_2\text{O}_3(l) \rightarrow (\text{CaO})_3 \cdot 2\text{Al}_2\text{O}_3(s) \quad (2-4)
\]

\[
4\text{CaO}(s) + 2\text{Al}_2\text{O}_3(l) + 2\text{Fe}_2\text{O}_3(l) \rightarrow (\text{CaO})_3 \cdot 2\text{Al}_2\text{O}_3 \cdot 2\text{Fe}_2\text{O}_3(s) \quad (2-5)
\]

Figure 2-1 shows the distribution of the different phases in the temperature range 300-1500 °C during heating and for 1500 to 1100 °C during cooling.

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\]

Above 1300 °C, the proportion of clinker liquid increases and nodules are formed. At the same time, intermediate phases dissociate to form liquid and belite. The belite reacts with free lime to form alite, according to reaction (2-3). A clinker temperature of about 1450 °C is required in order to obtain a proper product quality. A proper clinker quality has an alite content of minimum 50 wt. % and a free lime content of maximum of 1.5 wt. % (Taylor, 1997).

\[
\text{CaO}(s) + (\text{CaO})_2 \cdot \text{SiO}_2(s) \rightarrow (\text{CaO})_3 \cdot \text{SiO}_2(s) \quad (2-3)
\]

The formation of solid aluminate and ferrite from the liquid phase takes place when the temperature drops to 1230 °C, according to reactions (2-4) and (2-5).

\[
3\text{CaO}(s) + \text{Al}_2\text{O}_3(l) \rightarrow (\text{CaO})_3 \cdot 2\text{Al}_2\text{O}_3(s) \quad (2-4)
\]

\[
4\text{CaO}(s) + 2\text{Al}_2\text{O}_3(l) + 2\text{Fe}_2\text{O}_3(l) \rightarrow (\text{CaO})_3 \cdot 2\text{Al}_2\text{O}_3 \cdot 2\text{Fe}_2\text{O}_3(s) \quad (2-5)
\]

Figure 2-1 shows the distribution of the different phases in the temperature range 300-1500 °C during heating and for 1500 to 1100 °C during cooling.
2.3 Cement Production

Cement is produced in a continuous process and can be produced by at least four different methods, respectively referred to as wet, semi-wet, semi-dry and dry. This thesis will focus on the dry process because it is the most common production process nowadays. A more comprehensive description of the different types of production processes can be found elsewhere (Labahn and Kohlaas, 1983; Peray and Waddell, 1972).

The cement production process can be divided into three consecutive parts: \(^1\) Preparation of the raw materials, \(^2\) pyro-processing, and \(^3\) clinker processing. A flow diagram for the pyro processing stage, consisting of the kiln system is shown in Figure 2-2.
2.3.1 Preparation of Raw Materials

The first step in the production of cement is the crushing of the raw materials to a particle size of about 25-100 mm. The raw materials are subsequently stored in separate tanks according to their composition. This facilitates and controls the continuous delivery of raw materials to the raw mill with the desired composition. In the raw mill, the raw materials are dried by hot flue gases from the kiln system and ground together in a defined and well-controlled proportion to produce the raw meal. The particle size of the ground raw material can vary from 5 to 125 μm (Bye, 1999). The fineness of the particles is important for reaching the desired reactivity and ensuring a good heating and calcination (Bhatty et al., 2011; Cembureau, 1999). The blended raw materials are stored in a silo before being fed into the kiln system. The silo can typically store raw material for several production days in order to provide a buffer to ensure a continuous cement production (Cembureau, 1999).
2.3.2 Pyro Processing

The pyro-processing step is the heart of cement production, and covers the thermal treatment of the raw material, necessary to obtain the cement clinker. It involves preheating of raw materials, calcination, clinker reactions, and cooling of the clinker. These steps take place in the kiln system, which consists of a preheater tower, a calciner, a rotary kiln, and a clinker cooler. A typical modern kiln system and its parts are schematically illustrated in Figure 2-3.

The raw materials, which are referred to as raw meal in the kiln system, are introduced to the preheater tower. A preheater tower consists of a series of 4-6 vertical cyclones and is arranged in a 50-120 m high tower structure. By direct contact with hot exhaust gases from the kiln flowing counter currently, the raw meal is heated. Thus, a part of the thermal energy is recovered in the system. The most common preheater tower is the five staged, meaning with 5 cyclones, where the first cyclone has a temperature of approximately 300 °C and the final cyclone has a temperature around 800-900 °C. The residence time in each cyclone step is approximately 8 seconds for the raw materials and 1-2 seconds for the hot flue gases. Overall, the raw materials pass through the preheating tower in less than a minute (Hewlett, 1998; Taylor, 1997).

The preheated raw meal is admitted to the calciner, which has a temperature of 850-900 °C and under these conditions the majority of the CaCO$_3$ will thermally decompose into CaO and CO$_2$. Hot air from the clinker cooler, so-called tertiary air, is utilized as combustion air in the calciner. The fuel consumption for calcination can account for up to 60 % of the fuel needed for cement production (Madlool et al., 2011). The calciner can be integrated into the kiln system as an In-Line Calciner (ILC), where the flue gas from the rotary kiln passes through the calciner, or as a Separate-Line Calciner (SLC), where the flue gas from the rotary kiln bypasses the calciner, and enters the preheater. The ILC-system minimizes the amount of gas flow through the rotary kiln and hence rotary kiln size reduction. In addition, good conditions for reduction of NO$_x$ produced in the rotary kiln are achieved (Jensen, 1999). On the other hand, in a SLC-configuration, fuel combustion takes place more rapidly, due to a higher O$_2$ concentration, and a smaller calciner volume is needed compared to the ILC-system, for a fixed residence time, since the amount of gas through the calciner is smaller (Jensen, 1999).

However, the solid residence time is lower in a SLC-system and the mass and the particle behaviours lowers heat transfer from gas to fuel particle (Larsen, 2007). This thesis will refer only to the ILC-configuration because it is the preferred and most common design nowadays.

The hot meal, i.e. calcined raw meal after the 5$^{th}$ stage cyclone, enters into the rotary kiln, and flows counter currently to the hot flue gases, that are produced by the kiln burner flame. The rotary kiln is a long tube which is inclined 1-4° with horizontal and rotates 1-5 rpm to ease mass transport (Taylor, 1997). The rotary kiln can be divided into three different zones, as illustrated in Figure 2-3. The material colder end is the inlet of hot meal into the rotary kiln. In the transition zone, the materials start to melt, and form the clinker nodules. The clinker
reactions take place in the burning zone, or the hot end of the rotary kiln, where the clinker achieves a temperature of up to 1450 °C.

The clinker is cooled down by atmospheric air in the clinker cooler, which is typically a grate cooler (Hewlett, 1998). In this manner, preheated combustion air is produced and returned to the process through the rotary kiln (for combustion of the main burner fuel as secondary air) and the calciner (for combustion of the calciner fuel, as tertiary air). Grate coolers provide the most efficient and most flexible heat recovery system for modern cement plants (Cembureau, 1999). Experience has shown that a rapid cooling down from 1450 to 1200 °C is advantageous in order to minimize the formation of secondary belite and free lime (Taylor, 1997; Hewlett 1998).

**Figure 2-3:** Scheme of a typical kiln system, specifying the nomenclature used for different parts.
Modern cement plants can have a bypass system for the process gases, in order to reduce the chloride concentration in the kiln. The bypass system comprises the steps of extracting a portion of kiln exhaust gases, cooling the extracted exhaust gases and separating the dust. The bypass starts at the gas extraction point, which is located at the kiln side of the riser duct. At this position, the kiln gases have a low dust concentration and high gaseous concentration of Cl (FLSmidth A/S, 2008). The extracted kiln gases containing Cl and kiln dust, are quenched by air, in order to initiate condensation of the chlorides, and facilitate the subsequent separation of chlorides from the gas. This separation takes place in an electrostatic precipitator or a baghouse filter (FLSmidth A/S, 2008). Typical bypass rates are of up to 15% for chlorine bypass (European IPPC, 2013).

The installation of the bypass requires additional capital investment and increases heat and material losses. The removal of hot gas by the bypass leads to higher specific heat consumption of about 6–12 MJ/ton clinker per cent of removed kiln inlet gas (European IPPC, 2013).

### 2.3.3 Clinker Processing

The cooled clinker has a variable particle size, typically a diameter between 3-25 mm (Taylor, 1997). The clinker may be stored in a clinker silo or it can be directly ground in a ball mill, which is a rotating horizontal steel tube filled with steel balls, or in a vertical mill. When the tube rotates, the steel balls tumble and crush the clinker into a fine powder with a particle size ranging mainly from 3 to 30 μm (Taylor, 1997). A small amount of gypsum is added during the final grinding to control the setting properties. Additives such as coal fly ash, sand or raw material may also be added in order to improve the strength properties of the cement or to make the cement production more sustainable (Hewlett, 1998). The final cement product is transported to a cement silo until it is packed and distributed.

### 2.3.4 Process Data Overview

Table 2-2 provides an overview of typical process data, for a modern calciner kiln, representative for an ILC-system. The process data consists of the temperatures and residence times for both the gas and solids, and the O₂ concentration in the gas phase.

<table>
<thead>
<tr>
<th>Material</th>
<th>Preheater</th>
<th>Calciner</th>
<th>Rotary kiln</th>
<th>Cooler</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas temperature [°C]</td>
<td>350-880</td>
<td>880-1100</td>
<td>1100-2000</td>
<td>1100-25</td>
</tr>
<tr>
<td>Gas residence time [s]</td>
<td>~5-10</td>
<td>~3-4</td>
<td>~5-10</td>
<td>~1</td>
</tr>
<tr>
<td>Material temperature [°C]</td>
<td>100-780</td>
<td>780-900</td>
<td>900-1450</td>
<td>1400-100</td>
</tr>
<tr>
<td>Material residence time [s]</td>
<td>~50</td>
<td>~5</td>
<td>15-30 min</td>
<td>~30 min</td>
</tr>
<tr>
<td>Gas O₂ concentration [vol. %]</td>
<td>~5-12</td>
<td>11-12</td>
<td>2-7</td>
<td>~21</td>
</tr>
</tbody>
</table>

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</tr>
<tr>
<td>Material residence time [s]</td>
<td>~50</td>
<td>~5</td>
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<td>~5-12</td>
<td>11-12</td>
<td>2-7</td>
<td>~21</td>
</tr>
</tbody>
</table>
The data for the temperatures of the gas and the materials is a consequence of the counter current flow. The solid material is heated from 100 °C in the preheater to 1450 °C in the burning zone of the rotary kiln, while the gas that flows in the opposite direction, enters at ambient temperature in the cooler and reaches 2000 °C in the rotary kiln. The gas temperature gradually decreases until 350 °C in the preheater. The cooled gas is usually used to preheat the cement raw materials in the raw mill and leaves to the stack at a temperature around 100 °C.

Atmospheric air, which contains 21 vol. % O₂, is introduced into the cooler and further used in the kiln system. The oxygen concentration decreases to 2-7 vol. % in the rotary kiln as the combustion proceeds. However, a fraction of the cooling combustion air is bypassed via the tertiary air duct from the cooler to the lower part of the calciner, where the oxygen content is around 11-12 vol. %. In the lower part of the calciner, the fuel is introduced without combustion air, which contributes to a low oxygen level. The oxygen level decreases in the rotary kiln due to the combustion process and the dilution with the CO₂ formed during the calcination. In the preheater section, the oxygen concentration is affected slightly by oxidation reactions in the raw meal. The reactions include formation of SO₂ from pyrite, recarbonation of CaO, formation of CaCO₃, and combustion of organic bound carbon.

2.4 Conclusions

The production of Portland cement is a highly energy-consuming process which consists of a three step process. The process can be divided into preparation of raw materials, clinker production, and cement grinding. The clinker production, which takes place in the kiln system, requires that the raw materials, which consist typically of a mixture of limestone, clay, and sand, are heated up to approx. 1450 °C in order to calcine limestone and facilitate the clinker reactions. The calcination is a very endothermic process which normally uses 50-60 % of the total energy required for the production of cement. Gas temperatures in the kiln system range from ambient temperatures up to 2000 °C and the oxygen levels range from 2 to 21 vol. %, depending on the position in the kiln system.

Portland clinker consists mainly of four different minerals, which are alite, belite, ferrite, and aluminate. A proper clinker quality has an alite content of minimum 50 wt. % and a free lime content of maximum of 1.5 wt. %. The main strength giving compounds in Portland cement are alite and belite.

2.5 References


3. Alternatives Fuels in the Cement Production

This chapter provides an insight in the use of alternative fuels in cement production. Sections 3.1 and 3.2 describe the general characteristics of alternative fuels and their combustion. Finally, section 3.3 outlines the existing technologies for combustion of alternative fuels.

3.1 Introduction

Cement production has depended mainly on the use of fossil fuels such as coal and petcoke. However, the utilization of secondary fuels or alternative fuels, such as car tires (Trezza and Scian, 2009), plastic waste, sewage sludge (Zabaniotou and Theofilou, 2008) and wood waste (Mackes and Lightburn, 2003), is continuously increasing due to environmental concerns and the increase of conventional fuels prices. One of the leading countries with respect to replacement of fossil fuels is Germany, where 63.1% of the thermal energy came from alternative fuel sources in 2013 (VDZ, 2012). Individual cement plants are reported to have alternative fuels energy shares higher than 80% (European IPPC, 2013). Alternative fuels cover a wide range of fuels ranging from fossil fuel based (e.g. waste oil and natural gas) and all non-fossil fuels, such as biomass based, and waste from other industries.

Alternative fuels can have different chemical and physical properties compared to fossil fuels. The most important fuel characteristics to consider, when selecting alternative fuels, are the heating value, the ash content and composition, the particle size, and the moisture content. The heterogeneity amongst the physical and chemical properties of alternative fuels affect both the thermal energy input and the process stability, such as possible fuel spillage and modification of the input of minor elements. Fuel spillage is considered when unburnt fuel drops into the material bed and this can happen in the kiln flame and in the calciner. The fuel ash, which is incorporated into the clinker chemistry, may modify the minor elements input, thus the composition balance of the raw materials needs to be readjusted. The different types of typical alternative fuels used in the cement industry can be grouped as shown in Table 3-1. Some of the most common alternative fuels are industrial and municipal waste, tire derived fuels, meat and bone meal, and wood waste.

Table 3-1: Grouping of typical alternative fuels used in cement production (Larsen, 2007; Murray and Price, 2008; Nielsen, 2012).

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<td>Pyrolysis gas</td>
</tr>
<tr>
<td>Refuse derived fuel (RDF)</td>
<td>Waste solvents</td>
<td>Refinery waste gas</td>
</tr>
<tr>
<td>Waste wood/saw dust</td>
<td>Wax suspension</td>
<td>Biogas</td>
</tr>
<tr>
<td>Tire derived fuel (TDF)</td>
<td>Petrochemical wastes</td>
<td></td>
</tr>
<tr>
<td>Agricultural waste</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>Plastic/paper/textile waste</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
There are numerous advantages of using alternative fuels, both for the cement industry, and from society's point of view in relation to the general waste problems (Pizant and Gauthier, 1997; Mokrzycki and Uliasz-Bochenczyk, 2003; Greco and Enfils, 2006). Some benefits of the substitution of fossil fuels by alternative fuels are:

- Reduction of fuel and production costs.
- Alternative fuels may be partly or fully CO$_2$-neutral.
- Waste is effectively utilized as energy.
- The ash residue is incorporated into the cement clinker.

However, the usage of alternative fuels has some general requirements, such as availability of large amounts, legislation and permissions before a specific alternative fuel can be used, logistics for transport and handling of the specific fuel. The usage of alternative fuels varies widely across regions and countries and depends on local conditions.

Fuel analyses of fossil fuels and some commonly used alternative fuels are presented in Table 3-2. The presented values are approximate and may deviate depending on source, local conditions, water content, pretreatment, etc. However, the tabulated values reflect the diversity amongst typical fuels utilized and give an estimation of heating value and elemental composition. The fraction of volatile matter and fixed carbon are important for the combustion characteristics. The most important differences between alternative fuels and fossil fuels are listed below, because these differences may have a significant impact on the combustion and cement production.

- Alternative fuels may have a significantly higher content of volatiles compared to the solid fossil fuels. In general, alternative fuels contain less sulfur, fixed carbon, and fuel-bound nitrogen, and have a higher oxygen and hydrogen content than fossil fuels.
- The ash content of alternative fuels is typically higher than for fossil fuels. The ash may introduce some new elements, which can interfere with the chemistry of the cement materials and affect the operation of the system. Furthermore, alternative fuels may contain different amounts of volatile elements, such as S, Cl, Na, K, and Hg.
- Alternative fuels often have high moisture content, which may increase the combustion time needed. Furthermore, some energy is consumed for heating and evaporation of water and the flue gas volume is increased. This may decrease the production capacity and negatively affect the process efficiency.
- The heating value of some alternative fuels may be significantly lower than typical fossil fuels, due to ash and moisture content and the chemical composition. This implies that higher fuel mass flows are needed to provide the same thermal input. The increase of volume (if the density of the fuel is low) together with the increased mass flow can cause handling and feeding problems.

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Alternative fuels may have different devolatilization and char oxidation kinetics than conventional fuels due to different chemical composition and structure. This may influence the fuel combustion time and NO\(_x\) emissions.

Moreover, the composition of alternative fuels is rarely constant, which will be reflected by inhomogeneous physical and chemical properties. These variations can affect emissions, process stability, and clinker quality. Another important difference with respect to fossil fuels is that alternative fuels may be introduced to the kiln system in the form of large particles in the range of millimetres and centimetres, while fossil fuels are typically introduced with a particle sieve residue of 2-20 % on a 90 \(\mu\)m sieve (Nørskov, 2012).

The use of alternative fuels has been shown not to increase the total emissions of pollutants compared to fossil fuels (Lemarchand, 2000; Karstensen, 2008; Lee et al., 2007; Prisciandaro et al., 2003; Realf et al., 2005; Wurst and Prey, 2003). However, the use of alternative fuels may have positive as well as negative effects on the emissions of gas pollutants (Tokheim, 2012). The cement plants located in the European Union, which are using alternative fuels, are subject to Directive 2010/75/EU about industrial emissions (Directive 2010/75/EU). The important emissions are SO\(_2\), NO\(_x\), HCl, HF, Hg, Tl, dioxins and furans, total organic carbon, and CO. Further information about the legislation of emissions and the emission limit of each compound can be found in the aforementioned European Directive, except CO emission limit, which is set by local authorities.

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### Table 3-2: Typical composition, proximate analysis and heating values of fossil and alternative fuels used in the cement production.

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<tr>
<th>Fuel</th>
<th>Proximate analysis [wt. % dry]</th>
<th>Ultimate analysis [wt. % dry]</th>
<th>LHV [MJ/kg]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>VM (%)</td>
<td>H (%)</td>
<td>C (%)</td>
<td>N (%)</td>
</tr>
<tr>
<td>Anthracite Coal</td>
<td>1.51</td>
<td>67.98</td>
<td>3.29</td>
<td>0.47</td>
</tr>
<tr>
<td>Bituminous coal</td>
<td>1.4</td>
<td>33.86</td>
<td>3.71</td>
<td>0.55</td>
</tr>
<tr>
<td>Lignite coal</td>
<td>2.67</td>
<td>39.40</td>
<td>4.21</td>
<td>2.45</td>
</tr>
<tr>
<td>Pet Coke</td>
<td>10.2</td>
<td>71.88</td>
<td>0.23</td>
<td>3.01</td>
</tr>
<tr>
<td>Charcoal</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Natural gas</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Pine wood</td>
<td>79.85</td>
<td>15.17</td>
<td>0.85</td>
<td>0.51</td>
</tr>
<tr>
<td>Straw</td>
<td>64.3-80.3</td>
<td>13-19.5</td>
<td>4.7-20.1</td>
<td>46-50</td>
</tr>
<tr>
<td>Rice husks</td>
<td>61-69</td>
<td>16-17</td>
<td>15-20</td>
<td>38-42</td>
</tr>
<tr>
<td>RDF*</td>
<td>60-84</td>
<td>2-16</td>
<td>8-12</td>
<td>42-65</td>
</tr>
<tr>
<td>TDF*</td>
<td>54-66</td>
<td>23-30</td>
<td>7-23</td>
<td>64-81</td>
</tr>
<tr>
<td>MMBF*</td>
<td>65-72</td>
<td>7-9.7</td>
<td>18-28</td>
<td>42-46</td>
</tr>
<tr>
<td>PE*</td>
<td>100</td>
<td>0</td>
<td>-0-0</td>
<td>86-14</td>
</tr>
<tr>
<td>PVC*</td>
<td>91-91</td>
<td>1</td>
<td>33-5</td>
<td>0-0</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>48-64</td>
<td>0.6</td>
<td>17-50</td>
<td>28-39</td>
</tr>
</tbody>
</table>

### Notes:


**Concentration in ppm weight basis, Chemical ash composition as wt. % Na2O and K2O, n.a.: not available**
3.2 Combustion of Alternative Fuels

Many cement plants utilize alternative fuels in the calciner and the main burner, and these two units have been subject to modifications in order to optimize the combustion of such alternative fuels. Despite these modifications, the usage of relatively small particles is required in the calciner and in the kiln burner to ensure a sufficient fuel combustion and the desired flame profile. A consequence of firing large alternative fuels particles in the calciner and main burner is that the combustion may not be complete and subsequently partially or unburned solid fuels may drop into the material bed. In addition, coarse alternative fuels are sometimes fired directly into the material inlet end of the rotary kiln, because this solution requires minimal shredding of the fuel. However, there are several challenges associated with the combustion of fuels in direct physical contact with the cement raw materials, which may lead to modifications of the process conditions, stability, and clinker quality.

Firstly, it is necessary to evaluate the reaction path encountered when the different solid fuels are converted during devolatilization and char combustion, as illustrated in Figure 3-1. This topic has been discussed in details by Larsen (2007) and Nielsen (2012). The conversion pathway of a fuel is important to know and be aware of in the cement industry, because it will influence the total conversion time. The size of the char particle and the time required to complete the char oxidation is determined by the pathway that the fuel follows. For example, the char particle following pathway I or F gets smaller and will convert faster than char particle following pathway H1 and H2.

![Figure 3-1: Main reaction pathways involved in the combustion process of a solid fuel particle (Larsen, 2007).](image-url)
Consequently, if the solid fuels do not reach full conversion in the calciner or in the flame of the main burner, the fuel particles may end up in the bed material and affect the process stability. The solid fuels can end up in the bed material in the rotary kiln in four different ways depending on whether the fuels are fired in the calciner, main burner or directly into the material inlet of the kiln (Nielsen, 2012). The four scenarios are illustrated in Figure 3-2 and outlined briefly below:

1. Large solid fuels particles with a considerable weight, which are fired in the calciner and cannot be carried upwards with the gas flow, may drop through the riser duct, and into the rotary kiln.
2. Large solid fuels particles fired through the kiln burners may not be completely combusted in the flame of the main burner, and fall into the bed material.
3. Small and unconverted solid fuel particles, which are light enough to be carried upwards with the gas flow through the calciner and transported into the cyclones, can fall into the kiln inlet with the calcined raw meal.
4. Coarse solid fuels may be fired directly into the rotary kiln material inlet end.

Figure 3-2: Illustrative scheme of the four scenarios, whereby solid fuels can drop into the bed material in the rotary kiln, modified from (Nielsen, 2012). The numbers from 1 to 4 refer to the scenarios described above.
When solid fuel particles are partly or fully combusted in the material inlet of the rotary kiln, three situations can occur.  
1) The particles can be fully covered by raw materials,  
2) the particles can be partly covered by raw materials, or  
3) the particles can be on top of the raw material bed. The position of the fuel particle controls the heating mechanism, the mass transfer of oxygen, and the mass transfer of devolatilization and combustion products. The three situations are illustrated in Figure 3-3, where the mechanisms of the heat transfer and mass transfer of oxygen are also stated. Due to the rotation of the kiln, both the cement raw materials and the solid fuel particles are constantly in motion and the particle will therefore not experience just one situation during its combustion, but a combination of the three situations.

![Figure 3-3: Graphical scheme of the three situations with corresponding heat transfer and mass transfer mechanisms that a fuel particle can experience, modified from (Nielsen, 2012).](image)

During the combustion of the fuel particles, volatile gases are released and further combusted in contact with the gas in the freeboard. The gases may be reducing agents, such as CO, H₂, and light hydrocarbons, causing local reducing conditions in the kiln bed material. If no oxygen is available around the fuel particle, the solid fuels will experience pyrolysis and the gases released will not be combusted until they reach the freeboard. The induced reductive conditions in the material inlet of the rotary kiln may affect the product quality by modification of the clinker chemistry and the process stability of the kiln system by an increase in the internal circulation of sulfur, chlorine, and alkali metal species. The circulation of sulfur, which will be further discussed in Chapter 4, is especially important. This thesis will primarily focus on the effects of the combustion of alternative fuels fired in the calciner and directly into the rotary kiln inlet end on the process operation. The effects of firing alternative fuels in the main burner have been investigated previously (Nørskov, 2012). The effect of alternative fuels on the clinker product (quality and chemistry) is outside the scope of this thesis.

In order to provide further insight into the effects and consequences of the combustion of alternative fuels on the kiln bed material, it is necessary to understand how different alternative fuels are converted in the laboratory and industrial scale during combustion. It is also important to be aware of the different compounds
released during devolatilization of different fuels, because these gaseous compounds play a main role in the reductive decomposition of sulfates, as described in section 3.2.2.

3.2.1 Combustion Studies of Alternative Fuels

An extensive parameter laboratory scale study using a high temperature rotary drum with conditions similar to the industrial rotary kiln material inlet has previously been conducted (Nielsen, 2012). The study investigated the combustion of tire rubber, polypropylene, petcoke and pine wood. In the experiments, real cement raw material was not used because of its sticky characteristics during heating, and inert sand was therefore used. The effects of fuel mass, particle shape and size were investigated, showing that the external surface area and the particle thickness are more important parameters for the conversion, time of devolatilization and char oxidation than the mass of the fuel sample.

For polypropylene (which doesn’t have fixed carbon) and the devolatilization period of the other fuels, the temperature was the major rate influencing parameter. The conversion time decreased as the temperature increased from 700 to 1000 °C.

The rotational speed was observed to have an effect on the conversion for the char oxidation of tire, wood, and petcoke, as the conversion time increased when the rotational speed was increased in the interval 20 rpm to 6 rpm. There was also a change in bed behavior which affected the mixing process. Experiments with different raw material particle sizes, with average size from 18 to 600 μm, showed that the char oxidation time was dependent on the particle size. The time to complete the char oxidation was longer for the fine raw materials than for the medium and coarse raw materials. This can be explained by the fact that the fine sand follows a slumping bed motion where the mixing is less efficient, which means that the fuel particles are in poor contact with oxygen from the freeboard gas. The char oxidation was found to vary with oxygen concentration in the freeboard gas, which is reasonable because char oxidation is dependent on diffusion of oxygen to the char surface.

Several industrial studies using alternative fuels have been reported in literature (Zabanistou and Theofilou, 2008; Li and Zhang, 2011). Zabanistou and Theofilou (2008) studied the usage of 7.5 wt. % wet sewage sludge (60-70 % moisture content) in a cement plant on Cyprus in which the sewage sludge was mixed with conventional solid petcoke. Subsequently, it was fed for drying and grinding in the coal mill. This procedure reduced the moisture content of the fuel to 1 %. In this way, no fuel costs were required for drying. The approach of mixing an alternative fuel and a fossil fuel have been applied in several studies (Mackes and Lighthurn, 2003; Kara et al., 2011) and have been found not to affect the clinker quality and the process stability.
Chapter 3: Alternative Fuels in the Cement Production

The study of Mackes and Lightburn (2003) used wood chips in a US based cement plant and reported that no operation problems were encountered when wood chips were pulverized and burned in combination with petcoke (ratio of 15% wood and 85% petcoke) through the burners in the calciner. Another industrial study burning alternative fuel (RDF based on 66 wt. % textile, 17 wt. % paper and 17 wt. % plastic) in the main burner was performed by Kara et al. (2011). The fuel mixture was added to the main fuel (petcoke) in ratios of 0, 8, 12, and 15%, and it was observed that the clinker produced was acceptable. However, RDF caused low flame temperature and high humidity content inside the kiln and these conditions were reflected by a decrease in NO\textsubscript{x} emissions with increasing amount of RDF (Kara et al., 2011).

3.2.2 Volatile Gases from Fuels

The identification of the gases released from different alternative fuels during devolatilization in an oxygen-lean environment or during pyrolysis (absence of oxygen, e.g. when the particle is buried in the bed material) is important to know because amongst these gases may be reducing agents, which can promote the sulfur release from the raw materials.

Several studies in the literature have analyzed and quantified the volatile composition of fuels (Di Blasi et al., 1999; Wang et al., 2003; Kyari et al., 2005; Ouiminga et al., 2009; Wu et al., 2009; Fu et al., 2011). It is possible to identify the volatiles of different fuels at different conditions (pyrolysis, combustion). However, the measurements produced by different studies are not directly comparable due to the differences in the experimental configurations (heat transfer mechanism from the heating system to the specimen), sample characteristics (size, shape, moisture content) and the focus of the investigation. Table 3-3 compares the main volatiles compounds of various alternative fuels, which may be used in the cement industry. The thermal treatment, the reactor type, and the temperature range of the study are also indicated. These investigations are further explained in the following subsections. The nitrogenous species analyzed in the studies have been neglected because they are not an active part of the sulfur chemistry.
ure of degradation (between 800 and 1000 ºC) before with increasing temperature. The formation of carbon dioxide increased especially from 950 °C pyrolysis gas yield increased with increasing temperatue. The study of isothermal pyrolysis of biomass (rice straw, pelletized corn cob, and pelletized corn straw) at 700, 800, and 900 °C by macro-thermal gravimetric analysis was carried out by Wu et al. (2009). The biomass pyrolysis gas yield increased with increasing temperature, i.e. for pelletized corn cob, from 67.2 to 91.2 % at 700 and 980 °C, respectively. About 30 % by volume of total volatile gas was light hydrocarbons, such as CH₄, C₂H₆, and C₃H₈. The CO₂ content decreased with increasing temperature, while the H₂ content increased as the temperature rose, for example from pelletized corn straw pyrolysis almost no H₂ was obtained at 700 °C and 980 °C.

### 3.2.2.1 Biomass

Ouiminga et al. (2009) characterized carbonaceous species from the pyrolysis of millet stalks in a tubular kiln. The kiln was pre-heated to the desired temperature of degradation (between 800 and 1000 °C) before introducing the fuel. The gaseous compounds from millet stalks were mainly CO and CO₂ for carbonaceous species. The CO formation increased significantly with increasing temperature. The formation of carbon dioxide increased especially from 950 to 1000 ºC and the formation of CH₄ remained constant from 900 to 1000 ºC. The total amount of volatile carbon also increased from 40 % of the total mass at 800 °C to 53.4 % at 1000 °C (Ouiminga et al., 2009).

The study of isothermal pyrolysis of biomass (rice straw, pelletized corn cob, and pelletized corn straw) at 700, 800, and 900 °C by macro-thermal gravimetric analysis was carried out by Wu et al. (2009). The biomass pyrolysis gas yield increased with increasing temperature, i.e. for pelletized corn cob, from 67.2 to 91.2 % at 700 and 980 °C, respectively. About 30 % by volume of total volatile gas was light hydrocarbons, such as CH₄, C₂H₆, and C₃H₈. The CO₂ content decreased with increasing temperature, while the H₂ content increased as the temperature rose, for example from pelletized corn straw pyrolysis almost no H₂ was obtained at 700 °C and...
increased to 6.5 % at 900 °C. The light hydrocarbons content decreased from 700 to 900 °C, because the hydrocarbons decomposed into more simple molecules such as CO, CO₂, and H₂.

Maize stalks, rice straw, cotton straw, and rice husk were pyrolyzed in order to study the effect of the temperature on gas composition and char structure (Fu et al., 2011). The experiments were performed using a fixed bed reactor at different temperatures ranging from 600 to 1000 °C. The main gases produced were CO, CO₂, CH₄, C₂H₆, ethane (C₂H₆), and ethylene (C₂H₄). Methane was the most abundant hydrocarbon. The CO and CH₄ content in the product gases increased significantly with increasing temperature from 600 to 1000 °C, i.e. for maize stalk from 45.4 to 59.7 vol. % for CO and from 15.0 and 19.7 vol. % for CH₄. The CO₂ concentration exhibited the opposite trend. The maximum release rate of CO₂, CO, and CH₄ increased significantly with temperature and the time to reach the maximum release rate became shorter. Ethane and ethylene were minor gas products and the concentration of H₂ was below the detection limit of the gas analyzer.

The pyrolysis of wood chips has been studied extensively (Di Blasi et al., 1999; Di Blasi et al., 2001; Di Blasi and Branca, 2001; Di Blasi, 2008). The product distribution and the gas composition was studied on a bench scale in the temperature range of 377-727 °C (Di Blasi et al., 1999). At all temperatures, the pyrolysis gas consisted mainly of CO (the largest contribution), CO₂, CH₄, and lower amounts of H₂ and C₂ hydrocarbons. At temperatures below 800 °C, the production of H₂ was negligible. It was also observed that the CO yield increased with increasing temperature, and the CO fraction decreased with increasing particle size (Jand and Foscolo, 2005).

### 3.2.2.2 Tires

The pyrolysis gas obtained by different rubber tires consisted mainly of CO₂, CH₄, H₂, C₂H₆, and C₃H₆, but propane, propene, butane, butene, butadiene, and CO have also been found. Overall, the results suggest that the yields of oil, gas, and char from the pyrolysis of tires are not significantly influenced by the type and origin of the tire. However, there are noticeable differences in the composition of the derived gases and oils (Kyari et al., 2005).

Fernandez et al. (2012) studied the pyrolysis of tire rubber at 550 and 900 °C using rubber tire granules and tire fibers obtained as a waste during grinding and shredding of scrap tires. The amount of CH₄ increased with increasing pyrolysis temperature, especially in the case of the rubber granules from 9.9 % of the composition of the gas at 550 °C to 24.1 % at 900 °C. The amount of C3 (propane and propene) did not vary with the temperature. The behavior of C2 (ethane and ethene) was different for the two types of wastes; it increased with temperature in the case of the tire granules and did not show any great variation in the case of the fibers. Sulfuric acid was also detected from tire granulate, because it originated from the decomposition of sulfurous compounds. Hydrogen sulfide did not vary with the pyrolysis temperature, indicating that the vulcanized structure of the rubber had already decomposed at 550 °C. The C4 components of the gas (butane, butene, and propane, propene, butane, butene, butadiene, and CO have also been found. Overall, the results suggest that the yields of oil, gas, and char from the pyrolysis of tires are not significantly influenced by the type and origin of the tire. However, there are noticeable differences in the composition of the derived gases and oils (Kyari et al., 2005).

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which lead to an increase in the amount of lighter hydrocarbons and H₂. For example, for tire granulate the C4 components contributed 38.1% of the composition of the gas at 550 °C and decreased to 24.8% at 900 °C, and for tires fibers the amount of C4 decreased from 28% at 550 °C and 25.6% at 900 °C.

3.2.2.3 Plastics

Pyrolysis gases from polyethylene (PE) plastic bags have been characterized by Ouiminga et al. (2009). More than 50% of the volatile carbon was predominantly expressed in the form of light (C₆H₄ and CH₄) and heavy (C₂H₆) hydrocarbons. The CO and CO₂ concentrations were 10 times lower than the concentration of hydrocarbons. The percentage of carbon converted to CO, CO₂, and CH₄ increased with increasing pyrolysis temperature, i.e., at 800 and 1000 °C the percentage of carbon in the form of CO, CO₂, and CH₄ was 0.3%, 0%, and 13% and 2%, 3%, and 23%, respectively.

The emissions of pollutants from batch combustion of polystyrene (PS), PE, and poly-vinyl chloride (PVC) from 500 to 1000 °C were studied by Wang et al. (2003). The emissions of light hydrocarbon from the combustion consisted mainly of CH₄, C₂H₆, C₂H₄, acrylene, propene, propylene, and butane. In the case of PE, CH₄, C₂H₆, C₂H₄, acrylene, and propylene were identified at all temperatures and C₂H₄ (ethylene) was the most abundant light hydrocarbon specie. In addition, propene was identified at 600 °C, and butane at 800 °C. The maximum CO₂ yield for PS and PE was around 1500 mg CO₂/g sample at 600 °C, and the CO₂ yield decreased with increasing temperature from 700 to 1000 °C. The highest CO emission with 150 mg CO/g sample was produced by PE, followed by PS with 80 mg CO/g sample, and in the case of PVC, the yield of CO peaked at 800 °C with 50 mg CO/g sample. The yields of CO did not change drastically with increasing temperature (Wang et al., 2003).

Pyrolysis studies of plastics and tires have been focusing on the emissions of poly-aromatic hydrocarbons (PAHs) which are considered harmful to the environment. Therefore, the main pyrolyzed gases have not been quantified (Font et al., 2004; Aracil et al., 2005; Kwon and Castaldi, 2012).

3.3 Technologies for Alternative Fuels Combustion

New types of combustion equipments have been developed in order to avoid operational process challenges when alternative fuels are used in the traditional firing points of cement plants and for optimizing the combustion of alternative fuels. The technologies for alternative fuel combustion can be divided into external reactors which are typically placed next to the calciner, kiln burners, and new kiln designs as emerging technologies.
3.3.1 External reactors

Different types of external reactors for treatment of alternative fuels have been developed and are used at some cement plants. The common concept is to use the high heating value gas in the calciner and incorporate solid residues into the cement chemistry.

3.3.1.1 Combustion Chambers

A combustion chamber, which is an external reactor attached to the calciner or preheater, is a design for combustion of large fuel particles. Many different designs have been developed (Gaser and Tadular, 2009; FLSmidth A/S, 2011; KHD Humboldt Wedag, 2012a; Tysenkrup Industrial solutions, 2014a) and the combustion chambers operate typically with an excess of air, using the air generated in the clinker cooler and extracted from the tertiary air duct. Two types of large combustion chambers, where lumpy alternative fuels can be fired and the fuel residence time can be varied, will be further described in this section.

The HOTDISC from FLSmidth A/S is a combustion chamber designed for combustion of large and lumpy solid alternative fuels. Figure 3-4 and Figure 3-5 show a cross-sectional view of the HOTDISC and its typical position in an ILC-system. In the HOTDISC chamber, alternative fuels are introduced into a slowly rotating disc, where the fuels burn under oxidizing conditions when meeting the hot tertiary air. The fuel residence time is typically 20-40 min and can be optimized by adjusting the rotational speed of the disc. Raw meal from the lower cyclone stages of the preheater is added in order to control the temperatures inside the HOTDISC (FLSmidth A/S, 2011).

Figure 3-4: Cross-sectional view of the HOTDISC combustion device (FLSmidth A/S, 2011).

Figure 3-5: Typical position of the HOTDISC installed in preheater of an ILC-system (FLSmidth A/S, 2011).
The step combustor from Tyssenkrup Polysius (Tyssenkrup Industrial solutions, 2014a) is a combustion chamber specifically developed for high feed rates of low calorific and large-sized alternative fuels. Figure 3-6 shows the different parts and the principle of the step combustor. The fuel is fed into the inlet by special screw conveyors and by the conveying pressure of the screws, the fuel is lifted to the first stage, where the material is heated due to the hot tertiary air flowing over the material. The fuel transport through the different steps is realized with pulse jets. As function of the alternative fuel quality, the transport and discharge rates in the step combustor can be separately controlled and retention time extended up to 15 minutes (Menzel et al., 2009).

![Figure 3-6: Principle of the step combustor (Tyssenkrup Industrial solutions, 2014a).](image)

### 3.3.1.2 Gasifiers

Fluidized bed gasifiers for alternative fuels are also used in the cement industry (Schmidthals, 2003). In the gasifiers, the fuel is pyrolized under low-oxygen conditions and the lean gas produced is subsequently fed to the calciner as fuel, while the solid residues (char and ashes) are used as raw materials for cement production. The gasifiers can handle a wide variety of waste, regardless of their calorific values, i.e. paper and plastic waste (Wirthwein et al., 2002), whole tires (Saito et al., 1987), and sewage sludge (Kawasaki Heavy industries, 2013).

The world’s largest gasification furnace is the Conch Kawasaki Kiln (Kawasaki Heavy industries, 2013), which is able to process 300 tons of waste per day.

### 3.3.2 Kiln burners

New kiln burners have been designed specially to combust alternative fuels and have been developed by many manufactures (FLSmidth A/S, 2008; Pillard Feuerungen GmbH, 2004; KHD Humboldt Wedag, 2012b; ThyssenKrupp industrial solutions, 2014b; Kaufmann, 2014). The new designs involve a compromise between

![Diagram of gasifier](image)
high substitution rates of alternative fuels and low NO\textsubscript{x} emissions (Hass et al., 1999). A detailed review of rotary kiln burner design configurations for alternative fuels co-firing may be found elsewhere (Emberger and Hoenig, 2011).

Oxygen enrichment in the rotary kiln is a new technology, which has been demonstrated on a commercial scale to increase the alternative fuel utilization, decrease emissions, and improve the kiln performance and productivity (Arslan et al., 2013; Leger and Friday, 2001). However, economic considerations have prevented this technology from becoming a generally accepted practice (Leger and Friday, 2001).

3.3.3 Emerging technologies

3.3.3.1 Pyrorotor

The Pyrorotor is an invention from KHD Humboldt Wedag, which has not currently been installed in any cement plant yet (Streit, 2004). It consists of a rotary kiln that is flanged in between the ILC-system and the tertiary air duct, as illustrated in Figure 3-7. The large alternative fuels particles can be introduced, together with raw meal to control the temperature, in the upper end of the Pyrorotor and are converted by their downward movement caused by the rotation.
3.3.3.2 New Kiln Concept

The New Kiln Concept is an invention from FLSmidth A/S, which is patented (Jensen et al., 2010) but not commercialized. The equipment consists of a cement kiln that allows separate introduction of the calcined raw material and the fuels, as illustrated in Figure 3-8. Both the calcined raw meal and the fuels are heated by hot gases coming from the kiln burner. The fuel introduced in the cold inlet of the rotary kiln will be converted before the calcined raw meal is introduced. Thereby, the contact with the calcined raw materials and the local reducing zones will be minimized. The gases formed during the combustion of the fuel introduced in the kiln may be utilized for additional process stages, such as the calciner. The ashes from the fuel may be utilized in the forming of cement clinker or extracted with the cement clinker (Jensen et al., 2010).

The usage of alternative fuels is increasing continuously due to environmental concerns and the increase of conventional fuel prices. The physical and chemical characteristics of alternative fuels are different from the ones of fossil fuels, examples include higher content of volatiles, moisture and ash, lower heating value and particle size. The introduction of alternative fuels has led to modifications of the traditional firing points and

3.4 Conclusions

The usage of alternative fuels is increasing continuously due to environmental concerns and the increase of conventional fuel prices. The physical and chemical characteristics of alternative fuels are different from the ones of fossil fuels, examples include higher content of volatiles, moisture and ash, lower heating value and particle size. The introduction of alternative fuels has led to modifications of the traditional firing points and
creation of new combustion equipments specialized for firing alternative fuels, such as external reactors, especially designed kiln burners, and new layouts of kiln systems, in order to optimize the combustion. However, large particles are often fired in the calciner, kiln burner and also directly into the material inlet end of the rotary kiln because this solution requires a minimum of investments. Subsequently, partially or unburned solid fuels end up in the bed material and cause local reducing conditions. The induced reductive conditions in the material inlet of the rotary kiln may affect the process stability of the kiln system due to an increase in the internal circulation of volatiles elements.

Combustion studies of alternative fuels have been reviewed in order to understand the consequences of combusting alternative fuels in cement plants. The main gases released under pyrolysis conditions from biomass and agricultural waste, have been identified as CO, CO₂, CH₄, and light hydrocarbons from tire rubber and plastics. The amount of CO released from biomass and plastics increased with increasing temperature from 800 to 1000 °C, and the same trend for CH₄ was observed with biomass and tires. For biomass, the yield of gas and the amount of H₂ released increased with increasing temperature and the fraction of CO decreased with increasing particle size. For tire rubber, sulfur species, such as H₂S and H₂SO₃, were also released due to its sulfur content from vulcanizers. Thereby, the amount of reducing agents increases as well as the gas yield with increasing pyrolysis temperature and these gaseous compounds play an important role in the reductive decomposition of sulfates.

3.5 References


Chapter 3: Alternative Fuels in the Cement Production


Chapter 3: Alternative Fuels in the Cement Production


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Chapter 3: Alternative Fuels in the Cement Production

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Schirmann, H.; KHD’s combustion chamber, rotary kiln burner and services for alternative fuels use in the cement industry- KHD Humboldt Wedag, 8th Global Cemfunds Conference and Exhibition, Vienna, Austria, 2014.


Chapter 3: Alternative Fuels in the Cement Production


4. Circulation of Inorganic Elements in the Kiln System

This chapter provides an insight into the inorganic chemistry in the cement kiln system. Sulfur, chlorine, sodium, and potassium are considered in this chapter, since these elements are strongly related to operational problems experienced in the kiln. The main focus is on sulfur, in section 4.4 and in further chapters, because this element is most strongly affected by combustion of solid fuels in direct contact with the bed material.

The chapter initially outlines a description of the circulation of each of the volatile elements and the transformations of the different species containing these elements at different locations in the cement plant. The consequences and process challenges related to the combustion of alternative fuels are further described in section 4.2, with a special focus to the modification of the sulfur circulation, since this element is mostly affected by combustion conditions. Finally, thermodynamic equilibrium calculations are applied to map theoretically the inorganic chemistry in the kiln system under different atmospheres.

4.1 Circulation of Volatiles Elements

The circulating or volatile elements are minor components introduced in the kiln system through the raw meal and the fuels. The volatile elements evaporate when exposed to high temperature in the burning zone and then subsequently condense on the incoming raw meal or on plant surfaces in the cooler parts of the kiln system. By repetitive evaporation and condensation, these elements circulate at different temperatures and locations of a cement plant. When they are present in high concentrations, they often cause difficulties in kiln operation due to material build-up and ring formation, which will be further described in section 4.2.

Table 4-1 lists the range of the concentrations of Na, K, Cl, and S found in different raw materials used in the cement industry. Sodium, potassium, and sulfur concentrations are usually expressed as oxides due to the elements analysis method. The concentrations of these elements found in fuels were presented in Table 3-2 in Chapter 3.

<table>
<thead>
<tr>
<th>Concentration [wt. %]</th>
<th>Raw materials</th>
<th>Clay, shale</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O</td>
<td>Limestone, marl, chalk</td>
<td>0.0-1.5</td>
<td>(Jawed and Skalny, 1977; Sturz et al., 1998; Bhatty et al., 2011; European IPPC, 2013)</td>
</tr>
<tr>
<td>K₂O</td>
<td></td>
<td>0.0-3.5</td>
<td>0.2-3.0</td>
</tr>
<tr>
<td>Cl</td>
<td></td>
<td>0.0-0.6</td>
<td>Traces</td>
</tr>
<tr>
<td>SO₃</td>
<td></td>
<td>0.0-0.7</td>
<td>0.0-0.5</td>
</tr>
</tbody>
</table>

Table 4-1: Concentrations of Na, K, Cl, and S in the different raw materials.

4.1 Circulation of Volatiles Elements

The circulating or volatile elements are minor components introduced in the kiln system through the raw meal and the fuels. The volatile elements evaporate when exposed to high temperature in the burning zone and then subsequently condense on the incoming raw meal or on plant surfaces in the cooler parts of the kiln system. By repetitive evaporation and condensation, these elements circulate at different temperatures and locations of a cement plant. When they are present in high concentrations, they often cause difficulties in kiln operation due to material build-up and ring formation, which will be further described in section 4.2.

Table 4-1 lists the range of the concentrations of Na, K, Cl, and S found in different raw materials used in the cement industry. Sodium, potassium, and sulfur concentrations are usually expressed as oxides due to the elements analysis method. The concentrations of these elements found in fuels were presented in Table 3-2 in Chapter 3.

<table>
<thead>
<tr>
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</tr>
</tbody>
</table>
4.1.1 Reaction Affinity between Volatile Elements

The circulating elements have a strong affinity for other elements, and form chemical species like chlorides and sulfates. The following order of affinity has been observed (Bhatty et al., 2011; Hewlett, 1998; Chinyama, 2011):

1. The chlorine reacts primarily with the alkalis, forming KCl and/or NaCl, typically in gas phase. The residual chlorine combines with calcium, forming CaCl₂(s/l). However, it is seldom that the input of chlorine is higher than the input of alkalis.

2. The excess alkali reacts with sulfur, forming K₂SO₄ and/or Na₂SO₄ in solid or gas phase. The residual alkalis combine with CO₂, forming K₂CO₃ and Na₂CO₃ (Glasser, 2011), or with moisture, thereby forming NaOH and KOH in gas phase. The alkalis can also be embedded in clinker minerals.

3. The excess of sulfur present as SO₃ and/or SO₂ in the gas will react with CaO(s), forming CaSO₄(s).

The quantification of the circulation is determined by the volatility, which indicates the portion that is volatilized in the kiln and therefore not leaves the kiln with the clinker. The volatility is described using evaporation factors for each compound varying from 1 to 0, where 1 means that all volatile compounds are evaporated, and 0 that none is evaporated and therefore all leaves with the clinker.

4.1.2 Circulation of Sulfur

The sulfur circulation is the most complex. An illustration of the sulfur containing species and their transformation at different locations in a cement plant is shown Figure 4.1.

Sulfur can be introduced to cement rotary kilns by either cement raw materials and/or by the fuels. Biomass fuels, such as wood waste and straw, contain between 5 to 10 times lower amounts of sulfur, as when compared to fossil fuels. Sulfur can also be found in waste derived fuels, e.g. in car tires as a vulcanizer.

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In the preheater system, the organic sulfur and the pyrite from the raw meal are oxidized, thereby releasing SO\(_2\) upon heating in an oxidizing environment. The oxidation of sulfur species (pyrite and organic sulfur impurities) occurs between 300 and 600 °C, which corresponds to the temperature in the first or second cyclone in a preheater tower (Klotz, 1997). The decomposition of pyrite has been reviewed by Hu et al. (2006a), who found that in an atmosphere containing oxygen, pyrite can decompose by direct oxidation (reaction (4-1)) or by thermal decomposition of pyrite to pyrrhotite and sulfur, followed by subsequent oxidation to SO\(_x\) (reaction (4-2)). Iron sulfates may also be formed as minor products during the oxidation of pyrite in a gas rich in SO\(_x\) at temperatures lower than 600-650 °C (Hu et al., 2006a).

\[
\begin{align*}
2\text{FeS}_2(s) + 3\text{SO}_2(g) &\rightarrow 2\text{FeO}_2(s) + 4\text{SO}_2(g) \quad \text{(4-1)} \\
2\text{FeS}_2(s) + 2\text{SO}_2(g) + 2(1-0.5x)\text{S}_2(g) &\rightarrow 2\text{FeO}_2(s) + 4\text{SO}_2(g) \quad \text{(4-2)}
\end{align*}
\]
The gases leaving the preheater tower are used for drying the raw materials in the raw meal mill and a portion of the SO\textsubscript{2} will be captured, and thereby the SO\textsubscript{2} emissions will be lowered. Of the sulfur entering with the raw meal in the form of pyrites, it is often assumed that 30-50 % will leave the preheater tower as SO\textsubscript{3} (Nielsen and Jepsen, 1990; Bech and Gundtoft, 1998; Salmento and Shenk, 2004), but SO\textsubscript{2} emission from stack will account for 15-30 % of the sulfur entering with the raw materials in the form of non-sulfates (Nielsen and Jepsen, 1990). However, incorrect estimations of SO\textsubscript{2} emissions can be led because the amount SO\textsubscript{2} leaving the preheater tower can range from 10 to 65 % (Salmento and Shenk, 2004).

The SO\textsubscript{3} coming from the rotary kiln or from the calciner fuel is let to the calciner, where the good gas-solid mixing and the temperature favor capture of the sulfur, which is nearly 100 % (Salmento and Shenk, 2004). The sulfation of CaO with SO\textsubscript{2} has been recognized as a complex, high-temperature, short-time heterogeneous process, limited by gas-phase and solid-phase diffusion, with simultaneous physical transformation of the solid. The sulfation process can follow a number of routes, and in the literature, there is a lack of agreement on the mechanism. Two possible routes of sulfation have been discussed by Moss (1970), who examined the sulfation mechanisms, if proceeded via formation of CaSO\textsubscript{4}, or via the conversion of SO\textsubscript{2} to SO\textsubscript{3} and this directly reacts with CaO to form CaSO\textsubscript{4}. The relevant chemical reactions are:

\[
\text{CaO}(s) + \text{SO}_2(g) \rightarrow \text{CaSO}_3(s) \quad (4-3)
\]

\[
\text{CaSO}_3(s) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CaSO}_4(s) \quad (4-4)
\]

or

\[
\text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{SO}_3(g) \quad (4-5)
\]

\[
\text{CaO}(s) + \text{SO}_3(g) \rightarrow \text{CaSO}_4(s) \quad (4-6)
\]

It was suggested that the reaction proceeds via the formation of CaSO\textsubscript{4} (i.e. reaction (4-3) and (4-4)), at temperatures lower than 850 °C, where CaSO\textsubscript{4} is thermally stable. While reactions (4-5) and (4-6) dominate at temperatures above 850 °C (Moss, 1970) and the formation of SO\textsubscript{3} increases with decreasing temperature favored below 1000 °C by gas phase equilibrium, see Figure A-1 in Appendix A. The second route has been supported by many authors (Burdett, 1980; Dam-Johansen and Østergaard, 1991; Hansen et al., 1993; Hu et al., 2006b), although it has been suggested that both mechanisms might take place (Lin, 1988). Hu et al. (2006b) discussed the influence of the reaction conditions, such as SO\textsubscript{2}, O\textsubscript{2}, CO\textsubscript{2}, and H\textsubscript{2}O gas concentrations, limestone properties, reaction mechanism and modeling of the direct sulfation reaction via the second route.

Kinetic studies have shown that the rate of reaction of CaO with SO\textsubscript{2}/O\textsubscript{2} mixture is similar to that of the direct reaction with SO\textsubscript{2} (Allen and Hayhurst, 1996; Qin, 1995). No literature has been found to measure the precise SO\textsubscript{2} concentration because calibration gases for SO\textsubscript{2} analyzers are not available in the market. Both routes may take place simultaneously, however this topic is out of the scope of this review.

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\]

or

\[
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Chapter 4: Circulation of Inorganic Elements in the Kiln System

Calcium sulfate, CaSO_4, is incorporated in the hot meal entering the rotary kiln where it is gradually heated. Sulfates combined with calcium and alkalis form liquid phase, so-called sulfate melt, at around 1200°C (Choi and Glasser, 1988). In the transient zone of the kiln, two immiscible liquids may occur at equilibrium: one is an oxide melt, containing Al_2O_3, Fe_2O_3, and SiO_2, and the other is a sulfate melt, in which Al_2O_3, Fe_2O_3, and SiO_2 are nearly insoluble (Bhattly et al., 2011; Glasser, 2011). The sulfate liquid phase contributes to ion mobility and promotes combination in the clinker formation as fluxing agents allowing a significant increase in the rate of reaction of the calcium silicates. In an absolutely homogeneous mixture, no liquid phases are formed below 1338°C (Lea and Parker, 1935; de la Torre et al., 2007), where an eutectic in CaO-Al_2O_3-Fe_2O_3-SiO_2 system exists. Nevertheless, local inhomogeneities in the raw meal mixture cause a shift of the eutectic toward lower temperatures (de la Torre et al., 2007). Further explanation on the clinker phases and liquid phase formation has been reviewed by Telschow et al. (2014).

In the burning zone, where the bed material reaches its maximum temperature of 1450°C, evaporation of sulfur takes place forming SO_2, K_2SO_4, and/or Na_2SO_4 in the gas phase. The alkali sulfates in the gas phase are transported with the hot gases and the dust, along the rotary kiln. Alkali sulfates condense on dust particles, entrained by the kiln gases. The condensation product obtained between 700 and 800°C is a melt, but at lower temperatures, condensation may result in a solid. Dust particles are incorporated in the solid stream in the calciner, and alkali sulfates enter then with the hot meal into the rotary kiln and are partly incorporated in the sulfate melt, thereby improving the chemical reactivity of the material in the kiln and lowering the viscosity of the melt, which can facilitate some of the clinker reactions (Choi and Glasser, 1988).

Thus, an internal sulfur cycle is established in the rotary kiln and the calciner, as illustrated in Figure 4-2; a Sankey diagram, in which the width of the lines, are proportional to mass flow. This is a schematic representation made by Nielsen and Jepsen (1990), using data from 12 preheater kiln systems in the US. The SO_3 coming from the kiln is absorbed by the raw meal in the calciner, and reincorporated in the solid stream that is introduced in the rotary kiln. Therefore, there is a significant circulation around the inlet of the rotary kiln and the calciner, considering both the incoming material and the outgoing kiln gases. The molar flow of sulfates in the kiln inlet is approx. three times the molar flow in the outlet (clinker).
The fraction of sulfur released as SO$_3$ depends on the sulfur to alkali ratio in the rotary kiln (Mortensen et al., 1998), which is defined in equation 4.1, and expresses the proportion of sulfur that can be bound with alkalis.

$$\frac{SO_3}{Alk} = \frac{\frac{w_{SO_3,LOI \text{ free}}}{M_{SO_3}}}{\frac{w_{SO_3,LOI \text{ free}}}{M_{SO_3}} + \alpha \frac{w_{K_2O,LOI \text{ free}}}{M_{K_2O}} + \frac{w_{Na_2O,LOI \text{ free}}}{M_{Na_2O}}}$$  \[4.1\]

where $M_i$ is the molar mass of the component $i$, $n$ is the fraction of Na$_2$O that reacts with SO$_3$, and $w_{i, LOI \text{ free}}$ is the total input concentrations of the specie $i$, being SO$_3$, K$_2$O and Na$_2$O (representing sulfur, potassium and sodium, respectively) in wt. % loss on ignition free base. The loss on ignition (LOI) indicates how complete the calcination processing is. By practical experience, $\alpha$ has the value of 0.5 because there is substantial excess of K$_2$O over Na$_2$O (Bhatty, 1995) and analyses of different clinker compositions have revealed that nearly the entire amount of potassium and half the amount of sodium forms sulfate (Jawed and Skalny, 1977; Hansen, 2003). The optimum SO$_3$/Alk is close to 1, for a low sulfur evaporation (Newkirk, 1951; Plang-ngern and Rattanussorn, 2003; Whitehopleman, 2011; Rahman and Krapkat, 2012) because there will be enough alkali metals for formation of alkali sulfates, rather than formation of free SO$_2$ (Mortensen et al., 1998). If SO$_3$/Alk is lower than 1, the sulfur is bound but there is an excess of alkali, which lead to alkali circulation forming KOH and NaOH in gas phase (Bhatty et al., 2011; Cemnet, 2012). If the ratio is higher than 1, there will be an amount of sulfur in the raw material which will not be covered by alkalis. The excess of sulfur in the raw
materials to form CaSO₄ is termed excess SO₃, usually expressed as g excess SO₃/100 kg clinker, and may be
calculated by the equation 4.2 (Fortsch and Smidth, 2004).

\[
\text{Excess SO}_3 = \frac{w_{\text{CaSO}_4}}{M_{\text{CaSO}_4}} + \frac{w_{\text{CaO}}}{M_{\text{CaO}}} - \alpha \left( \frac{M_{\text{CaSO}_4}}{M_{\text{CaO}}} \right) w_{\text{LOI,free}}
\]  

[4.2]

The limit on excess sulfur is given to be in the range of 250-600 g/100 kg clinker (Fortsch and Smidth, 2004;
Cemnet, 2004). The lower limit is for low burnability raw meal, and the upper limit is for high burnability raw
meal. The burnability is a measurement of how easy/difficult the clinker phases are formed. The excess sulfur
will form CaSO₄, which is least thermally stable sulfate and will be contributing to a higher evaporation factor.

The sulfur volatility depends on the SO₃/Alk ratio and also on the operating conditions of the kiln, i.e.:

- Oxygen content of the kiln atmosphere. Deficiency of oxygen or local reducing kiln atmosphere
  increases the volatility of sulfur, because low oxygen level shifts reaction (4-7).

\[
\text{CaSO}_4(s) \rightarrow \text{CaO}(s) + \frac{1}{2} \text{SO}_3(g) + \frac{1}{2} \text{O}_2(g)
\]  

(4-7)

The variation of the oxygen content in the kiln inlet has shown to modify the SO₃ concentration
measured in the bypass gas, which is extracted from the kiln inlet. The relationship between SO₃ bypass
emissions and O₂ concentration in the kiln inlet of the rotary kiln is shown in Figure 4-3. At higher O₂ concentrations,
the SO₃ evaporation gets suppressed, and there will be no SO₃ emission in the bypass stack representing the SO₃ concentration in the material inlet of the rotary kiln. However, when the oxygen level in the kiln material inlet gets below around 2 vol. %, the sulfur evaporation increases steeply, and the bypass emissions can increase significantly (Steuch and Johansen, 1990). At lower oxygen concentrations, reduced sulfur species such as H₂S, COS in presence of carbon, and SOCl₂ in presence of Cl may also be formed, however, these species are not measured in cement plants.
Chapter 4: Circulation of Inorganic Elements in the Kiln System

4.3.1 Temperature in the burning zone. The volatility of the sulfur species is increasing as a function of temperature. Thermal decomposition is avoided by lowering the burning zone temperature. This may be achieved by making the raw meal more chemically reactive (burnability), which means finer grinding of the raw meal or adjusting the chemical composition of the raw meal. If the raw meal has a low burnability, it needs higher temperatures in order to get a low free lime in the clinker. Therefore, raw materials with low burnability or high temperatures overheating the clinker have a high impact on sulfur volatility (Hewlett, 1998; Smith, 2012).

The sulfur volatility can also be modified by carbon from fuels in the bed material, which will be further explained in section 4.3.2 and 4.3.3. Under stable operational conditions, and if there is enough alkali available to combine with the sulfur input, the volatility of the sulfur can vary from 0.35 to 0.6 (Bhatty et al., 2011).

During nodulization, the sulfate melt can be trapped in the inner core of the clinker nodules (Christensen and Johansen, 1979). The sulfate melt reaching the cooler will subsequently crystallize in the clinker. The composition of the sulfate melt at the end of the burning zone will determine the mixture of compounds that will solidify according to the tertiary diagram of CaSO₄-K₂SO₄-Na₂SO₄, illustrated in Figure 4-4. It can be seen that there are three primary precipitation areas, corresponding to CaSO₄, K₂SO₄·2CaSO₄ (calcium langbeinite) and (K,Na,Ca)SO₄ (aphthitalite). If the composition of the melt is located in one of precipitation areas, the species of that area will precipitate first.

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Sulfur in the Portland cement clinker is mainly found as Na₂SO₄, K₂SO₄, CaSO₄, (KₓNaₙ)SO₄ (aphthitalite), K₂SO₄·2CaSO₄ (calcium langbeinite), and as substituents in the major clinker phases, mainly alite and belite with little in the ferrite (Twomey et al., 2004; Pollitt and Brown, 1969). For most common Portland cement, the upper acceptable limit of sulfur expressed as SO₃ in clinker, in order to assure good quality is 1.6 wt.% (Farag and Kamel, 1994; Cemnet, 2013). More than half of the sulfur originating from raw materials and fuel appears in the clinker; the rest is lost in the flue gas and in the kiln dust (Jawed and Skalny, 1977).

Larger amounts of sulfur, higher than 2.6 wt.% SO₃ in clinker (Uda et al., 1998), start to negatively influence on the clinker mineral formation, via the inhibition of alite formation, and promoting the stabilization of belite and free lime, which needs to be lower than 1.5 wt.% CaO in clinker. One measure to prevent this phenomenon is to add calcium fluoride (CaF₂) to the raw meal, as a mineralizer. This allows lowering the burning temperature, and consequently the formation of alite is accelerated and the burnability is improved. However, concentrations higher than 0.25 wt.% CaF₂ in clinker are negatively affecting the cement properties such as retarded setting, reduced early strength and increased late strength (Klemm et al., 1979; Ghosh, 1991; Bhatty, 1995; Bhatty et al., 2011).

4.1.3 Circulation of Chlorine

The chlorine circulation and the locations of the formation of different chlorine species in a cement plant are illustrated in Figure 4-5.

The chlorine, as chlorides, is frequently found in limestone and clays, predominantly as NaCl. The raw material meal usually contains relatively small amounts of Cl, mostly less than 0.01 wt.% LOI free (Bhatty, 1995) and...
Chlorine can be liberated during combustion of fuels, and the chlorine input from fuels can vary significantly, depending on the type of fuel. The Cl-content in fossil fuels, such as coal and petcoke, is rather low, but it can be significant for alternative fuels, such as RDF, see Table 3-2. The possible paths and release mechanisms of Cl during pyrolysis and combustion of biomass are explained elsewhere (Johansen et al., 2013). HCl gas is produced when fuels containing organically bound chlorine or inorganic chloride salts are burned (Partanen, 2004). Organically associated Cl can also be released in the gas phase as CH₃Cl (Sahel et al., 2014). In the calciner, and along lower preheater stages, the HCl will be absorbed by free lime according to reaction (4-8) (Partanen, 2004), however the absorption of HCl by limestone is strongly dependent on the humidity of the flue gas. The absorption of HCl by limestone has been extensively studied by Partanen et al. (2005a, 2005b, 2005c).
\[ \text{CaO(s)} + 2\text{HCl(g)} \rightarrow \text{H}_2\text{O(g)} + \text{CaCl}_2(\text{s}) \] (4-8)

In the burning zone, there is no reactive free CaO suspended in the flame, and HCl from kiln fuel will therefore go directly to the preheater and be converted to CaCl\(_2\) there.

In the calciner and the lower cyclone stages, at a temperature between 800-850 °C, the chlorine species from the raw materials can melt, and the condensation of chlorine species from the kiln gases also occur. Therefore, the chlorine species are present in the liquid phase. The inverse reaction of (4-8), can also occur in presence of moisture.

In the burning zone, KCl and NaCl as chlorine compounds evaporate from the sulfate melt. The chlorine has an evaporation factor range of 0.900 to 0.996, and will evaporate nearly 100 % (Bhattly, 1995; Jøns and Østergaard, 2003; Jøns et al., 2008). The boiling temperatures of KCl and NaCl are approximately 1400 °C at 1 atm. The circulation is determined by the phase equilibrium between liquid and gaseous KCl.

Figure 4-6 shows a Sankey diagram for chlorine circulation showing how the gaseous, liquid, and solid chloride flows. The Sankey diagram was made based on data from a Finnish cement plant, and the diagram is only valid for low chlorine circulation (Jøns, 2013). The chloride has a considerable circulation around the calciner leading to high chlorine concentration. As an approximation, the chlorine mass flow in the kiln inlet is 200 times greater than the discharged mass flow in the outlet.
High values of the SO/Alk ratio are critical in combination with circulation of chlorides, because the sulfidation of alkali chlorides at temperature higher than 900 °C can take place according to the general reaction (4-9), where M can be Na or K. Alkali sulfates can be either solid or gaseous depending on the temperature and whether aerosol formation occurs or not, i.e. dependent on the local concentration and temperature profiles. Reaction (4-10) shows the sulfation of CaCl2, which can also react with SO3. The combination of HCl and SO3 in presence of moisture, in the gas phase makes the kiln gas very corrosive and sulfation is enhanced by the presence of chlorides in the middle zone of the kiln (Jøns and Østergård, 2001). The same gas combination is responsible for deposit build-ups on the riser duct and/or cyclones caused by formation of chloroellestadite (Bhatty et al., 2011), see section 4.2.5.

\[
2\text{MCl}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) + \text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{M}_2\text{SO}_4(\text{g}) + 2\text{HCl}(\text{g})
\]  
\[
\text{CaCl}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) + \text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CaSO}_4(\text{g}) + 2\text{HCl}(\text{g})
\]  

(4-9) (4-10)

Hydrolysis of alkali chlorides in the gas phase contributes to the formation of HCl(g), according to reaction (4-11) especially at temperatures of the burning zone. However, the formation of HCl through this reaction at temperatures below 1000-1150 °C is limited, because the majority of the KCl is in gas phase, and the tendency for KCl (g) to hydrolyze at such temperatures is low (Jøns and Østergård, 2001).

\[
\text{KCl}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{KOH}(\text{g}) + 2\text{HCl}(\text{g})
\]  
\[
(4-11)
\]

The chlorine can be found in the clinker as CaCl2, and sometimes as KCl, if it is trapped in the inner core of the clinker nodules. Most of the standards for Portland cement restrict the amount of chloride present to 0.1 wt. %, in order to avoid problems of reinforcement corrosion in concrete (Hewlett, 1998; Dalton et al., 2004; Farag and Kamel, 1994).

### 4.1.4 Circulation of Alkalis

Circulation of alkalis, which are mainly introduced from the raw materials, is represented in Figure 4-7. It is well known, that potassium species are usually more volatile than the sodium species (Bhatty, 1995), see Figure 4-8. The intensity of the alkali cycle depends upon the nature of the alkali metals in the raw material, on operating practices, and on type of kiln (Bucchi, 1981). The limiting content of Na2O and K2O is generally expressed as Na2O equivalent, which is defined by equation 4.3.

\[
W_{\text{Na}_2\text{O equiv}} = W_{\text{Na}_2\text{O,LOI free}} + \frac{M_{\text{Na}_2\text{O}}}{M_{\text{K}_2\text{O}}} W_{\text{K}_2\text{O,LOI free}}
\]  
\[
[4.3]
\]
The source of alkali is most commonly clay or shale, but they can also be present in some limestone, sand, and frequently in various types of alternative raw materials such as fly ashes. The average alkali concentrations are 0.17 wt. % Na2O and 0.57 wt. % K2O for the raw materials (Bhatty, 1995). In most cases the alkali input by fossil fuels and/or by alternative fuels is rather small or negligible, except for cases with high alkali content in the ash, i.e. bituminous coal (Vassilev and Vassileva, 2009).

In the preheater tower, the alkalis partly dissociate into the gas phase, and recombine with other elements according to the affinity order, described in section 4.1.1. If the alkalis are not balanced by sulfates, they will remain very volatile and accumulate in the circulation between the kiln and the preheater. The extent of alkali volatilization varies with raw materials, and is higher for clays than for feldspars. About 50 wt. % of alkalis present in the raw feed are volatilized in the kiln, between 800 and 1000 °C (Jawed and Skalny, 1977).
The acceptable range of Na$_2$O and K$_2$O concentration in the kiln riser, varies from 3 to 5 wt. % LOI free (Bhatty et al., 2011). Excess alkalis have a potential to form alkali carbonates in the cyclones. Furthermore, too high alkali content without sulfur coverage can also cause build-ups in the kiln riser, or blockages in the tertiary air pipe, as mentioned in the circulation of sulfur (section 4.1.2).

The alkali sulfates form part of the sulfate melt and remains trapped in the nodules as a liquid through the burning process. Clinker nodules more porous tends to contain high alkali sulfates (Harrison, 2009). Studies on the distributions of alkalies in the clinker have confirmed that finer nodules contain lower alkali levels than coarser nodules due to the higher surface available for alkali volatilization (Harrison, 2009; Masaki et al., 2002; Samet and Sarkar, 1997). In the burning zone, the alkali can evaporate as NaCl, KCl, NaOH, KOH, K$_2$SO$_4$, and/or Na$_2$SO$_4$, as shown in Figure 4-7. Presence of H$_2$O (g) in the kiln atmosphere promotes the formation of alkali hydroxides, which are more volatile than the corresponding sulfates, according to reaction (4-12). A similar reaction also takes place for sodium.

$$H_2O(g) + 2K_2SO_4(g) \rightarrow 4KOH(g) + 2SO_2(g) + O_2(g)$$  \hspace{1cm} (4-12)

The rest of the alkalis not being in the gas phase recombines directly in the bed material with Cl or S, or are integrated into the lattice of the clinker minerals, such as belite and aluminate.

Alkali sulfates condense on dust particles at the exit gas temperature of the rotary kiln. Furthermore, raw meal is added in the riser duct in order to favor the alkali sulfate condensation, otherwise, the alkali sulfates would condensate on the walls of the riser duct, creating deposits. In this way, alkali sulfates in gas phase from the kiln are incorporated in the raw meal after the calciner (Jensen, 2014). Too high alkali content without sulfur coverage can also cause build-ups in the riser or blockages in the tertiary air duct.

The composition of the condensate is not be pure alkali sulfate but may include CO$_2$ from the gas stream and the clinker meal. Thus, the chemistry of the melt is an alkali sulfate and alkali carbonate melt, containing small amounts of alkali hydroxide. The presence of carbonate dissolved in the molten sulfate phase explains the presence of CO$_2$ in the clinker analyses (Bhatty et al., 2011).

In the presence of chlorides and sulfates, the volatilization behavior of both Na and K is modified greatly (depending on how Na and K are combined) as shown by the vapor pressure-kiln temperature relationship in Figure 4-8. In the presence of sulfur, alkalis preferentially form sulfates, if present in amounts higher than the required stoichiometric balance (Bhatty et al., 2011).
Chapter 4: Circulation of Inorganic Elements in the Kiln System

4.2 Consequences of High Volatile Circulation

4.2.1 Deposit Build-up Formation

The consequences of high internal circulation of elements are formation of build-up and blockages. The gaseous species condense in the cooler zones, and the condensation products are often chemically aggressive and with low melting temperature range. Therefore, the liquid is present in the preheater tower, the presence of which, reduces the flowability of raw meal, and causes the particles to stick to the walls (Smith, 2012). This may subsequently cause build-up on cyclone walls and riser ducts. Formation of build-ups may reduce the kiln

Some of the Na₂O and K₂O are incorporated into aluminate, ferrite and belite and the residual alkalis will remain as sulfates. Introduction of alkalis into clinker minerals modifies their crystal structure, which may decrease the hydraulic reactivity of the cement (Jawed and Skalny, 1977). Alkali compounds in the clinker can be divided into three main groups: 1) alkali sulfates, 2) alkali aluminates and aluminoferrites, and 3) alkali silicates. In some cases, alkali may also occur in the form of carbonates (Jawed and Skalny, 1977).

High levels of total alkali in the final cement often lead to higher pH, and better early strength development, but lower later strengths. Soluble alkalis, which are not bound with sulfur, may cause flash set (rapid and early loss of cement workability during water addition), due to activation of the calcium aluminates, and will also cause a significant loss of 28 days strength (Midgley, 1984). Alkalis potentially can give rise to cracking and expansion in concretes, due to their deleterious alkali-silica reaction with reactive aggregates. In this situation, the alkalis react with moisture, and produce a gel which expands (Hewlett, 1998; British ecological survey, 2005). Furthermore, high concentration of alkalis in concrete has harmful effects on most mechanical properties of concrete, such as compressive, splitting, direct tensile, and flexure strengths (Smaoui et al., 2005).
production, and cause higher heat consumption, and kiln or plant stops, which are expensive. Table 4-2 lists the common intermediate compounds found in build-ups and kiln rings and their typical location. Table 4-2: Common intermediate compounds found in build-ups and kiln rings (Saint-Jean et al., 2005; Nievoll et al., 2009).

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Location typically found</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spurrite</td>
<td>(2CaO·SiO$_2$·CaCO$_3$)</td>
<td>Lower cyclones</td>
</tr>
<tr>
<td>Ellestadite</td>
<td>Ca$_2$Z(SiO$_4$)$_2$(SO$_4$)$_Z$</td>
<td>Riser duct</td>
</tr>
<tr>
<td>Sulfospurrite</td>
<td>(2CaO·SiO$_2$·CaS$O_3$)</td>
<td>Kiln rings</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>CaSO$_4$</td>
<td>Cyclones and riser duct</td>
</tr>
</tbody>
</table>

In the literature, chemical analysis of the build-up samples from different cement kiln preheaters have shown that the main constituents are SO$_4$, K$_2$O, CaO and Cl$^-$ and that their proportions may vary significantly, depending on their location (Recio Dominguez et al., 2010). The dominant phases in most of the samples were CaSO$_4$ or a mixture of CaSO$_4$ and CaCO$_3$. Smaller amounts of other phases, such as ellestadite solid solution (Ca$_2$Z(SiO$_4$)$_2$(SO$_4$)$_Z$ where Z can be OH, F, or Cl$^-$), more frequently chlorellestadite, Ca$_2$(SiO$_4$)$_2$(SO$_4$)(Cl$^-$), and spurrite have also been reported. Microstructural examination showed that the growth of the rings was due to successive deposition of particles and condensation of gases. The study stated that the main cause of the deposit formation was the presence of a glassy phase, $K_r$ Na$_2$Cl (Recio Dominguez et al., 2010). The presence of spurrite and KCl were found to be the reasons for the build-up stability in the lower part of the preheater (Kurdowski and Sobon, 1999). The investigation suggested a KCl crystallization model based on a vapor-liquid-solid (VLS) mechanism, which is illustrated in Figure 4-9. The first step is the condensation of volatile elements on the grains of limestone; then agglomerates are formed in the presence of a liquid phase, and stick to the walls of the gas ducts, causing further increase in thickness of the solid material layer. Then, in the accretion formed, good conditions are created for KCl crystallization according to the VLS mechanism, i.e. KCl vapor pressure of and a temperature close to the melting point (Kurdowski and Sobon, 1999).
The composition of the build-ups has been further investigated by Saint-Jean et al. (2005), using X-ray fluorescence (XRF), scanning electron microscopy (SEM), and chloride potentiometric titration. Based on the analyses, it was found that the corrosion scale contained water-insoluble as well as water-soluble chlorine. Build-ups on the walls of cyclones, and the riser duct, contained substantial amounts of chlorine in water-insoluble form, identified as chlorellestadite instead of the more common water-soluble KCl and NaCl. The chlorellestadite formation might lead to the clogging of pipes, which results in a decreased clinker output, and necessitate cleaning. Based on thermodynamic calculations, Saint-Jean et al. (2005) proposed that the chlorellestadite was formed due to the presence of gaseous HCl, and the reaction (4-8) which becomes more favored, as the temperature decreases. Consequently, the presence of chlorellestadite indicates formation of HCl in the hot atmosphere (Saint-Jean et al., 2005).

\[ \text{CaO}(s) + 2\text{HCl}(g) \rightarrow \text{H}_2\text{O}(g) + \text{CaCl}_2(s) + \text{Cl}_2(g) \]  

(4-8)

The degree of contact between the gas and lime-containing dust in the kiln may influence the HCl formation (Saint-Jean et al., 2005). It was proposed two reactions, (4-13) and (4-14), which can take place in the cooler parts of the kiln depending on the extent of contact of the gases with lime-containing dust (Saint-Jean, 2003).
Chapter 4: Circulation of Inorganic Elements in the Kiln System

Insufficient dust contact:
\[ SO_2(g) + 2KCl(g) + H_2O(g) + \frac{1}{2}O_2(g) \rightarrow K_2SO_4(l) + 2HCl(g) \]  \hspace{1cm} (4-13)

Sufficient dust contact:
\[ SO_2(g) + 2KCl(g) + CaO(s) + \frac{1}{2}O_2(g) \rightarrow CaSO_4(s) + 2KCl(g) \]  \hspace{1cm} (4-14)

According to the insufficient dust contact reaction, the poor contact between the hot kiln gases and lime-containing dust in the kiln causes formation of gaseous HCl from KCl and SO\(_2\), and subsequently, HCl in contact with the hot meal in the preheater unit can form chlorellstadite (Saint Jean, 2003). Figure 4-10 and Figure 4-11 illustrate the global equilibrium analyses simulating the reactions with sufficient and insufficient contact with lime-containing dust, respectively. The system was modeled as an enclosed box of variable volume with a fixed pressure of 1 atm and considered two phases: pure solid (chlorides and sulfates) and an ideal gas (N\(_2\), CO\(_2\), O\(_2\), and H\(_2\)O). A third phase, which consisted on CaO (s) representing the dust, was only included for the case of the sufficient contact with lime containing dust (Figure 4-10).

Analyzing the results with decreasing temperature (from 1400 to 1000 \(^\circ\)C), at high temperature there is SO\(_2\) (g) due to the thermal decomposition in the burning zone for both cases. For the case of sufficient contact with dust, the SO\(_2\) concentration decreases to zero below 1200 \(^\circ\)C because it is captured by the lime-containing dust.

In addition, no HCl in the gas phase is observed. On the contrary, for the case of insufficient contact with dust, not all the SO\(_2\) in gas phase is not absorbed by CaO when decreasing temperature and below 1200 \(^\circ\)C, formation of alkali sulfates and HCl (g) occurs. Figure 4-11, for the case of insufficient contact with dust, shows that SO\(_2\)

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and HCl in the gas phase will be observed in the kiln inlet. Jean et al. (2005) concluded that the HCl (g) concentration can be reduced by means of better gas-solid contact in the kiln.

Sulfur and chlorine concentrations in the hot meal can be used to evaluate the risk of build-up formation in the calciner, according to Figure 4-12 (Enders, 2011). The diagram is based on industrial experience, and is divided in 3 zones: low, medium and strong build-up tendency. The build-up tendency is linked to the required cleaning or removal of the build-ups. Therefore, it is recommended to operate a cement plant in the low and medium build-up tendency zones.

According to Figure 4-12, the hot meal content of SO$_3$ should be maintained below 6 wt. %, and the Cl content below 3.5 wt. %, in order to avoid strong coating tendency.

It is generally accepted, and in agreement with Table 4-2, that the formation of build-ups in the lower cyclones may be associated with an increase in chlorine evaporation, and the build-ups in the riser duct with an increase in sulfur evaporation.

### 4.2.2 Coating and Ring Formation in Rotary Kilns

Blockages in the kiln system are normally referred to as either coating or ring formation (Peray and Waddell, 1972), consisting of a mass of clinker or dust that adheres to the wall of the kiln, and solidifies state. They are easily formed, when an excess of sulfur over alkalis exists in the kiln atmosphere.

There are different types of kiln rings and their difference is based on their composition and location in the kiln. Figure 4-13 illustrates a rotary kiln with five typical complications, which are:
Chapter 4: Circulation of Inorganic Elements in the Kiln System

1. Nose rings or ash rings
2. Clinker coating
3. Trumpet coating or sinter ring
4. Clinker rings
5. Transition zone rings

Figure 4-13: Illustration of the five typical coating complications in a cement rotary kiln.

The nose ring, which is marked by point 1 in Figure 4-13, is formed in the hot burning zone, where the clinker leaves. It can be formed very fast, and sometimes needs daily removal. These formations are caused by crystallization of clinker liquid, or free alkali sulfates in the clinker. The liquid available at the kiln nose permits adherence of the dust particles, and therefore the building of the nose ring continues. Microscopic evaluations of clinker produced during the presence of a nose ring, indicate the presence of slow cooling. Slowly cooled clinker causes the alite to revert back to belite and free lime (Hamilton, 1997). The build-up in the clinker cooler back wall, referred as snowman build-up, is illustrated in Figure 4-14, and is caused by the same problem that promotes the nose ring, which is a slow cooling of the clinker.

Figure 4-14: Illustration of the snowman build-up on the clinker cooler back wall, adapted from (Hamilton, 1997).

Point 2 in Figure 4-13 shows the clinker coating, which normally has the same chemistry and mineralogy as the clinker bed, since it is made up of the clinker. It is desired to operate the kiln with coating formation in order to protect the lining from thermal shocks, abrasion by the kiln bed and chemical infiltration by the gases, and prolong the lifetime of the kiln (Clark, 2011). The thickness of the coating is under normal conditions determined by the heat transfer through the lining which means that when the surface temperature of the lining reaches the melting point of the clinker liquid, it stops growing in thickness. Thus, an equilibrium exists at

Figure 4-15: Illustration of the snowman build-up on the clinker cooler back wall, adapted from (Hamilton, 1997).
these conditions. Figure 4-15 shows the influence of the temperature on the coating in the rotary kiln. In scenario A, the rotary kiln has a thick coating layer that may continue to grow in thickness until the equilibrium temperature is reached. Scenario C shows a kiln with a hot flame, and the coating layer is seen to become liquefied and drop off the refractory lining. If the thickness of the coating layer becomes too low, it will decrease the refractory lifetime. The surface temperature is the most important factor in the formation of a coating, since the flame shape governs the surface temperature at all points in the burning zone. For that reason, the flame has a considerable effect on the coating formation (Peray and Waddell 1972). The amount and the properties of the liquid phase will also affect the ability to form the coating (Clark, 2011).

Point 3 of Figure 4-13 marks the position in the rotary kiln, where the burning zone starts. The coating composition is similar to the clinker, because this coating is established where the liquid phase begins to form but the melt comes into contact with a cooler surface and solidifies, thereby binding clinker particles together (Hewlett 1998). Changes in operational temperature can lead to coating formation at one location, which will later come off, when the temperature is changed. Repetitive shedding of coatings and formation of too much coating may lead to ring formations (Peray and Waddell, 1972).

Changes in operation temperatures can lead to coating formation at one temperature, which will later come off, when the temperature is changed. Frequent falling out of coatings and the formation of too much coating can lead to ring formations (Peray and Waddell, 1972).

Point 4 of Figure 4-13 shows the clinker rings that form inside the kiln. Clinker rings are characterized by their relatively high content of alite and aluminate. They are typically caused by recirculation of clinker dust in the combustion product gases from the main burner. These rings can be avoided by eliminating the dust recirculation from the cooler or by adjustment of the main burner to produce a short and dense flame (Clark, 2011).
The rings in the kiln inlet zone, called transition zone rings, are showed by point 5 of Figure 4-13. These rings do not contain aluminate, and only very little alite (Palmer, 1990). The composition of transition zone rings is often quite complex, and they are associated with operating conditions, such as high concentrations of alkali chlorides in the kiln gas, or reducing condition in the material kiln bed.

Reducing conditions, raw meals with difficult burnability, flame shape, and burner position are known to increase the amount of sulfur in the kiln atmosphere, thereby favoring ring formation (Nievoll et al., 2009). Sulfospurrite appears to be the mineral phase responsible for ring formation in the cement preheater kilns (Nievoll et al., 2009). Sulfospurrite crystals have been found on the surface of the refractory lining, and subsequent rapid growth of the ring, in a SO\textsubscript{3} rich kiln atmosphere, is probably enhanced by the liquid double sulfate 2CaSO\textsubscript{4}K\textsubscript{2}SO\textsubscript{4} (Ca-langbeinite). The analyzed samples showed an internal variability, which reflected the variations in composition and temperature of the kiln gases (Recio Domínguez et al., 2010). The same study tested different refractory materials against ring formation, and concluded that SiO\textsubscript{2} impregnated alumina bricks impeded sulfospurrite crystallization by stabilizing belite very efficiently.

Kiln rings in a preheater kiln system are not as frequent as in previous kiln systems due to the improvements in manufacturing technology, operation control, and raw materials and clinker homogeneity (Herfort et al., 2010). These improvements have also resulted in significant improvements in product performance. The operation process parameters experience nowadays less variation, this can be illustrated for example in Figure 4-16, showing the variation of lime saturation factor (LSF) for three different rotary kilns. The LSF is the ratio of CaO to the other three main oxides, and controls the ratio of alite to belite in the clinker. The clinker produced in batches in bottle kilns in the nineteen century were very heterogeneous as the raw materials. The oldest kiln from 1890, presents a big variation of the LSF percentage in short periods of time, and this large variability was causing operational problems, because the clinker was produced in batches in bottle kilns were very heterogeneous as well as the raw materials. The introduction of rotary kilns facilitated the blending and uniformity of the raw materials. In the long kiln, where calcination was taking place inside the rotary kiln, the process parameters showed still significant variation, but the variability has been significantly reduced for the actual preheater kilns, which show the improvement on operational control. For that reason, kiln rings are rarely formed in the actual preheater kiln systems.

Chapter 4: Circulation of Inorganic Elements in the Kiln System

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4.2.3 Shell Corrosion and Refractory Deterioration

The combined presence of SO$_2$ and HCl makes the kiln gas very corrosive (Jøns and Østergaard, 2001). Consequently, the presence of reducing atmospheres coupled with a high sulfur level in the kiln system, may lead to refractory deterioration and corrosion of rotary kiln shells and calciner shells, which subsequently result in high maintenance costs.

Jøns and Østergaard (2001) studied kiln shell corrosion in 12 suspension calciner kilns and found that the corrosion was restricted to a short zone, located from the start of the kiln coating, to 10-20 m in the direction of the kiln inlet. Severe corrosion occurred when the kiln gas contained high levels of both sulfur and chlorine.

The corrosion products were found to be brittle, and porous, with chlorides and alkali metals present in different amounts and homogenously distributed. However, it was not possible to link the composition of the corrosion product to the position where the sample was taken.

The corrosion reactions on kiln shell are proposed to be chain reactions (Lai, 1990; Jøns and Østergård, 2001).

First, the release of HCl in gas phase takes place by reactions (4-11) and (4-15), occurring in the kiln, where thermally unstable alkali chlorides are transformed to more stable alkali sulfates. Hydrochloric acid can penetrate through the refractory and due to the decrease in temperature, chlorine formation proceeds via reaction (4-16). According to Jøns and Østergård (2001), a temperature gradient, which is established by the lining and the porous deposit, will be formed between the kiln atmosphere and the kiln shell. The elemental chlorine can chemically interact with the metal shell by chlorination of iron, reaction (4-17). Subsequently, the oxidation of FeCl$_2$, the hydrolysis of FeCl$_3$, and sulfidation of iron continue by reactions (4-18), (4-19), and (4-20), respectively.
Chapter 4: Circulation of Inorganic Elements in the Kiln System

The chlorine gas is believed to be the main promoter of corrosion since it increases the porosity of the corrosion layer, thus decreasing the diffusion resistance, and thereby making the kiln more vulnerable to further attacks (Jøns and Østergård, 2001). A schematic representation of the shell corrosion is presented in Figure 4-17, where it can be observed the different compounds that may be formed in the shell plate causing corrosion. Two types of corrosion are observed: 1) corrosion during kiln operation resulting in scaling of the kiln shell, which is the oxidation of the metallic iron by dry gases (containing S and/or Cl) at elevated temperatures, also known as high temperature corrosion; and 2) rusting during kiln shut downs caused by condensation or absorption of moisture.

Experiences from different plants have revealed that as long as chlorine is not present, the corrosion rate stays at an acceptable level, i.e. 1/3 mm per year (Karlsson, 2013). The corrosion rate is calculated for the thinnest

Figure 4-17: Schematic mechanism of shell corrosion, modified from (Kötter and Bartha, 1987).
part of the kiln shell, which limits the lifetime of the kiln shell. Assuming a thickness of 25 mm for the thin part, this kiln shell can be worn down by corrosion to 12 mm before the stresses become too high, and the process of thinning down takes 30 to 40 years (Holtmann, 1995).

The calciner corrosion is believed to be caused by the increased sulfur circulation, which penetrates into the refractory material. Sulfur compounds may react with humidity and subsequently\( \text{H}_2\text{SO}_3\) may condense on the inner steel shell (Jensen, 2012). Figure 4-18 illustrates schematically the mechanism of corrosion due to the infiltration of corrosive gases, such as \( \text{SO}_2\) and \( \text{HCl} \), through the pore structure of the refractory lining or through joints penetrating the outside steel shell (Lechtenberg and Diller 2012).

Refractory can fail due to chemical attack because brick reaction with clinker melt and alkali salts can occur. The intensity of the chemical attack increases with temperature, time and proximity to the burning zone. The disposal of alternative fuels in cement kilns has intensified chemical attack to the lining in all kiln zones, including the preheater and cooler (Szczerba, 2009; Vadász et al., 2009).

### 4.3 Circulation of Volatile Elements due to Combustion of Alternative Fuels

Alternative fuels have different characteristics compared to fossil fuels. Their utilization in the cement manufacturing may therefore have several effects on the process stability, such as reducing conditions, poor heat distribution, unstable pre-calciner operation, blockages in the preheater cyclones, build-ups in the kiln riser ducts, higher \( \text{SO}_2\), \( \text{NO}_x \) and \( \text{CO} \) emissions and dusty kilns (Nielsen, 2012). Furthermore, the type of fuel used may introduce specific material components or increase the concentration of specific elements, which can interfere with the chemistry/quality of the cement, refractory life, gas and material flow or potential emissions to the atmosphere, and thereby affect the operation of the system.
In the following section, the introduction or increase of elements in the cement chemistry coming from alternative fuels is explained, but it is not described in detail because the topic is outside of the scope of the project.

### 4.3.1 Introduction or Increase of Elements in the Cement Chemistry

The main elements introduced with alternative fuels are: Na, K, Cl, Zn, P, Fe, Si found as SiO₂, and carbon in cases of incomplete combustion. Furthermore, heavy metals such as As, Cd, Cr, Pb, Hg, Cu, Ni, and Sn may be incorporated as traces. The presence of heavy metals in the clinker does not affect the quality when the amount is under a threshold limit. Trace elements exceeding the threshold limit may affect the clinker, e.g. Cu affects the alite formation, while Zn will affect aluminate (Gineys et al., 2011). However, heavy metals are one of the major hazards in the flue gas from alternative fuels, due to environmental implications. Mercury and Cd are examples of heavy metals, which tend to be highly volatile at burning zone temperatures (Conesa et al., 2008).

Alternative fuels that contain Fe (e.g. TDF, up to 25 wt. % for truck tires (Nielsen, 2012)) or silica (e.g. ash from rice husks, which contain 70-90 % silica (Chiyama, 2011)) contribute to the main oxides of the clinker, and their required content in the raw materials should therefore be reduced.

The clinker quality may also be negatively affected, if the clinker is exposed to reducing conditions induced by the alternative fuel if combusted in direct contact with the material bed in the rotary kiln. The main problem is the reduction of Fe₂O₃ to FeO, which takes place at temperature higher than 450 °C, or to elemental Fe, which occurs under strongly reducing conditions. FeO, which has Fe in the oxidation state +II, catalyzes the decomposition of alite and reduces the ferrite content. This leads to modifications of the Portland cement properties, and potential color change. This phenomenon is known as brown clinker (Klaus, 2000). The clinker quality may also be negatively affected by the addition of metal oxide residues (Trezza and Scian, 2000) and waste material ashes (Karagiannis et al., 2008; Pipilikaki et al., 2005; Trezza and Scian, 2005; Trezza and Scian, 2009) to the clinker during the clinker processing through combustion of alternative fuels if the raw meal mixtures is not adjusted accordingly.

### 4.3.2 Local Reducing Conditions

The kiln atmosphere is oxidizing in order to produce a good quality cement clinker and ensure a proper combustion of the fuel (Hewlett, 1998). However, when there is fuel spillage from the calciner and/or main burner, and/or fuel are fired into the rotary kiln material inlet end, it can consume oxygen locally and thereby cause local reducing conditions that may have a negative effect on the clinker quality and the process stability. Only the effects on the process stability are considered in this thesis. It should be emphasized that reducing conditions in the material kiln bed do not necessarily mean reducing conditions in the gas phase and vice versa.

In the following section, the introduction or increase of elements in the cement chemistry coming from alternative fuels is explained, but it is not described in detail because the topic is outside of the scope of the project.

### 4.3.1 Introduction or Increase of Elements in the Cement Chemistry

The main elements introduced with alternative fuels are: Na, K, Cl, Zn, P, Fe, Si found as SiO₂, and carbon in cases of incomplete combustion. Furthermore, heavy metals such as As, Cd, Cr, Pb, Hg, Cu, Ni, and Sn may be incorporated as traces. The presence of heavy metals in the clinker does not affect the quality when the amount is under a threshold limit. Trace elements exceeding the threshold limit may affect the clinker, e.g. Cu affects the alite formation, while Zn will affect aluminate (Gineys et al., 2011). However, heavy metals are one of the major hazards in the flue gas from alternative fuels, due to environmental implications. Mercury and Cd are examples of heavy metals, which tend to be highly volatile at burning zone temperatures (Conesa et al., 2008).

Alternative fuels that contain Fe (e.g. TDF, up to 25 wt. % for truck tires (Nielsen, 2012)) or silica (e.g. ash from rice husks, which contain 70-90 % silica (Chiyama, 2011)) contribute to the main oxides of the clinker, and their required content in the raw materials should therefore be reduced.

The clinker quality may also be negatively affected, if the clinker is exposed to reducing conditions induced by the alternative fuel if combusted in direct contact with the material bed in the rotary kiln. The main problem is the reduction of Fe₂O₃ to FeO, which takes place at temperature higher than 450 °C, or to elemental Fe, which occurs under strongly reducing conditions. FeO, which has Fe in the oxidation state +II, catalyzes the decomposition of alite and reduces the ferrite content. This leads to modifications of the Portland cement properties, and potential color change. This phenomenon is known as brown clinker (Klaus, 2000). The clinker quality may also be negatively affected by the addition of metal oxide residues (Trezza and Scian, 2000) and waste material ashes (Karagiannis et al., 2008; Pipilikaki et al., 2005; Trezza and Scian, 2005; Trezza and Scian, 2009) to the clinker during the clinker processing through combustion of alternative fuels if the raw meal mixtures is not adjusted accordingly.

### 4.3.2 Local Reducing Conditions

The kiln atmosphere is oxidizing in order to produce a good quality cement clinker and ensure a proper combustion of the fuel (Hewlett, 1998). However, when there is fuel spillage from the calciner and/or main burner, and/or fuel are fired into the rotary kiln material inlet end, it can consume oxygen locally and thereby cause local reducing conditions that may have a negative effect on the clinker quality and the process stability. Only the effects on the process stability are considered in this thesis. It should be emphasized that reducing conditions in the material kiln bed do not necessarily mean reducing conditions in the gas phase and vice versa.
The process stability is mainly affected by the increase in sulfur release from the raw meal to the gas phase. The sulfur release in the kiln inlet comes mainly from the decomposition of CaSO\(_4\), by the reducing agents released by the fuels, so-called reductive decomposition of CaSO\(_4\), which will be further discussed in Chapters 5 and 6. The partial or unburned alternative fuels increase the content of solid carbon, especially CO (g) and can react as follows.

\[
\text{CaSO}_4(s) + C(s) \rightarrow \text{CaO}(s) + \text{SO}_2(g) + \text{CO}(g) \quad (4-21)
\]

\[
\text{CaSO}_4(s) + \text{CO}(g) \rightarrow \text{CaO}(s) + \widetilde{\text{SO}}_3(g) + \text{CO}_2(g) \quad (4-22)
\]

Similar reactions apply for the alkali sulfates. However, these compounds are thermally more stable than CaSO\(_4\). The alkali sulfates may decompose and release both sulfur and alkali metals to the gas phase when fuels fired by the kiln burner fall into the material kiln bed, which is one of the scenarios illustrated in Figure 3-2.

Reducing conditions promote \(\text{SO}_2\) release and tend to increase the intensity of the sulfur cycle in the kiln system. Therefore, the reducing conditions may alter the material circulation considerably and cause operational problems.

### 4.3.3 Increase of Circulation Phenomena in the Kiln System

Sulfur and chlorine circulation may often be increased due to the utilization of alternative fuels. High concentrations of these compounds often cause difficulties in kiln operation with build-ups, mainly in the preheater and the kiln inlet section. The intensity of the cycles varies between different systems, and there are also considerable variations within one single kiln system, depending on the operating conditions.

#### 4.3.3.1 Sulfur Circulation

Incomplete combustion of fuels, when they are burned in direct contact with the bed material, can cause an increase of sulfur circulation because reducing agents, which promote the reductive decomposition of CaSO\(_4\), are formed during the combustion in an oxygen-lean environment. Normally, the increase of sulfur circulation is associated to alternative fuels due to their physical and chemical properties differences with fossil fuels (particle size, moisture content, and others mentioned in Chapter 3) and their place of firing. While fossil fuels do not theoretically give rise to sulfur circulation because they are finely grind, which causes full combustion in the calciner or in the main burner. However, an increase of sulfur circulation when petcoke char was combusted in contact with the kiln inlet material bed, has been experienced.

In an industrial cement plant, which was burning pellets of dried sewage sludge through the main burner, the sulfur evaporation has a decreasing linear tendency with the \(\text{O}_2\) concentration in the gas phase at the kiln.
material inlet, see Figure 4-19. Increasing the oxygen content at the kiln material inlet minimizes the sulfur evaporation. The increase of oxygen concentration is believed to reduce the occurrence of local reducing condition in the clinker bed where unburned sewage sludge were dropped from the flame (Nørskov, 2012).

![Figure 4-19: Sulfur evaporation factor as function of O\textsubscript{2} exhaust gas concentration measured at the kiln material inlet during firing 0.5-2 tons per hour dried sewage sludge in the kiln burner (Nørskov, 2012).]

In the calciner, the fuel and the raw meal is in direct contact, but the SO\textsubscript{2} release is not taking place there. It has been suggested that partly calcined hot meal is less problematic than completely calcined hot meal with regards to sulfur release, since the endothermic calcination reaction will absorb heat developed from the fuels and thereby prevent temperature increment that leads to sulfur release. However, there is a lack of understanding and experimental results in this area.

4.3.3.2 Chlorine Circulation

Alternative fuels, RDF in particular, may introduce up to 4 wt. % chlorine. The growing use of alternative fuels is increasing the input of chlorine. Some of the waste plastics, such as PVC, sewage sludge, meat and bone meal, and chlorinated hydrocarbons may increase the amount of chlorine introduced into the system significantly. The circulation of chlorine is determined by the phase equilibrium between liquid and gaseous KCl. The evaporation generally occurs in the burning zone of the kiln and the re-condensation in the riser pipes and lower cyclones, where Cl can combine with alkalis and sulfates and form mixtures with a low melting point. The degree of volatile recycling within the system will increase with increasing amounts of alkali chlorides. Too high Cl is influencing the economy of clinker production by causing kiln stoppages, corrosion, and uneven clinker quality.

Under unfavorable circumstances, some of the chlorine, which is normally present in the kiln atmosphere in the form of NaCl and KCl, can be replaced by HCl. The hydrochloric acid can cause corrosion of the steel material inlet, see Figure 4-19. Increasing the oxygen content at the kiln material inlet minimizes the sulfur evaporation. The increase of oxygen concentration is believed to reduce the occurrence of local reducing condition in the clinker bed where unburned sewage sludge were dropped from the flame (Nørskov, 2012).

![Figure 4-19: Sulfur evaporation factor as function of O\textsubscript{2} exhaust gas concentration measured at the kiln material inlet during firing 0.5-2 tons per hour dried sewage sludge in the kiln burner (Nørskov, 2012).]

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Under unfavorable circumstances, some of the chlorine, which is normally present in the kiln atmosphere in the form of NaCl and KCl, can be replaced by HCl. The hydrochloric acid can cause corrosion of the steel
walls of the rotary kiln (Saint-Jean et al., 2005). A bypass can be a very effective way of removing chlorides from the kiln system. Approximately 90% of chlorine can be removed by extracting 5% of kiln exhaust gas, but no more than 15% of alkalis or sulfur can be removed (Sutou et al., 1999).

The effects of chloride are strongly influenced by the sulfur load in the kiln (Jøns et al., 2008). A model of the chloride circulation in the kiln and how this is influenced by the S load based on simple thermodynamic considerations was developed by Jøns et al. (2008). The findings were supported by statistical treatment of data collected from more than 50 modern kiln systems. It was concluded that the higher the sulfate content in clinker, the lower the evaporation factor for chlorine.

4.4 Thermodynamic Calculations

For a better understanding of the inorganic chemistry in the rotary kiln, thermodynamic equilibrium calculations were performed using the commercially available software FactSage 6.2 (Bale et al., 2009). This program uses the principle of minimization of the total Gibbs free energy to calculate the equilibrium composition of a chemical system with known composition, temperature and pressure. The principle of the Gibbs energy minimization is described in Appendix A.

4.4.1 System considering inorganic chemistry with clinker chemistry

A system model including the inorganic chemistry with the clinker chemistry is first considered. Two groups of compounds are differentiated in the bed material: Group 1) containing the elements (Ca, Si, Al, Fe) present in the clinker compounds and Group 2) the volatile elements described in section 4.1. The two groups of solid compounds interact between each other and also with the gas phase. The system examines the equilibrium between the gas species and the solid species in the bed material and also the equilibrium between the solid compounds of the bed. This equilibrium is schematically illustrated in Figure 4-20:

![Figure 4-20: Schematic view of the gas and bed material in equilibrium.](image)

4.4.1.1 Assumptions and Limitations

The equilibrium model is based on the composition of hot meal and the flue gas leaving the rotary kiln. The hot meal composition in weight percentage and in mol/kg clinker, from Nielsen (2012), is shown in Table 4-3. Nielsen (2012) specified that the defined hot meal contains a relatively high amount of Cl and S, relative to the guidelines for a stable kiln operation. MnO, TiO₂, SiO₂, MgO and P₂O₅ are specified but they are
The composition of the hot meal is traditionally expressed as oxides (Table 4-3), however, the oxides are not the compounds present in the hot meal. Therefore, based on the molar amount of S, K, Na, Si, Al, Fe, Cl and Ca, the compound concentrations, such as Na₂SO₄, K₂SO₄, CaSO₄, KC, Ca₃SiO₅ (belite)₁, SiO₂, Al₂O₃, Fe₂O₃, and CaO, in the hot meal can be calculated and used as input for the thermodynamic calculations. The aforementioned compounds with their corresponding concentrations are listed in Table 4-4. The values represent typical values found in the kiln inlet of a cement rotary kiln. All the compounds are inserted in the calculations as mol/kg clinker.

The flue gas in the kiln is characterized to be oxidizing. The composition and concentration of the gas used for the thermodynamic calculation of the full system is specified in Table 4-5. The values represent typical values found in the kiln inlet of a cement rotary kiln. All the compounds are inserted in the calculations as mol/kg clinker.

---

₁ The formation of belite starts at temperatures above 700 °C, as it is assumed that part of the silica content is contributed by belite.

---

Table 4-3: Typical composition of hot meal used in the equilibrium calculations (Nielsen, 2012).

<table>
<thead>
<tr>
<th>Hot meal compound</th>
<th>Concentration [wt. %]</th>
<th>Concentration [mol/kg clinker]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>18.00</td>
<td>3.080</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.76</td>
<td>0.467</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.30</td>
<td>0.144</td>
</tr>
<tr>
<td>CaO</td>
<td>56.80</td>
<td>10.128</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.50</td>
<td>0.286</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.20</td>
<td>0.032</td>
</tr>
<tr>
<td>SiO₂</td>
<td>6.12</td>
<td>0.765</td>
</tr>
<tr>
<td>MnO</td>
<td>0.05</td>
<td>No included</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.25</td>
<td>No included</td>
</tr>
<tr>
<td>SrO</td>
<td>0.09</td>
<td>No included</td>
</tr>
<tr>
<td>MgO</td>
<td>1.86</td>
<td>No included</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.07</td>
<td>No included</td>
</tr>
<tr>
<td>LOI, 975 °C</td>
<td>5.77</td>
<td>No included</td>
</tr>
</tbody>
</table>

Total 99.94 -

Table 4-4: Specific concentration of Na₂SO₄, K₂SO₄, CaSO₄, KC, Ca₃SiO₅ (belite)₁, SiO₂, Al₂O₃, Fe₂O₃, and CaO in the hot meal.

<table>
<thead>
<tr>
<th>Hot meal compounds</th>
<th>Concentration [mol/kg clinker]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂SO₄</td>
<td>0.032</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>0.101</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>0.632</td>
</tr>
<tr>
<td>KC</td>
<td>0.330</td>
</tr>
<tr>
<td>Ca₃SiO₅ (belite)₁</td>
<td>1.000</td>
</tr>
<tr>
<td>SiO₂</td>
<td>2.000</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.467</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.632</td>
</tr>
<tr>
<td>CaO</td>
<td>7.497</td>
</tr>
</tbody>
</table>

Total 99.94 -

Table 4-5: Typical composition of hot meal used in the equilibrium calculations (Nielsen, 2012).

<table>
<thead>
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</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.30</td>
<td>0.144</td>
</tr>
<tr>
<td>CaO</td>
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<td>10.128</td>
</tr>
<tr>
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<td>0.286</td>
</tr>
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<td>0.032</td>
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</tr>
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<tr>
<td>TiO₂</td>
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<td>No included</td>
</tr>
<tr>
<td>SrO</td>
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<td>No included</td>
</tr>
<tr>
<td>MgO</td>
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<td>No included</td>
</tr>
<tr>
<td>P₂O₅</td>
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<td>No included</td>
</tr>
<tr>
<td>LOI, 975 °C</td>
<td>5.77</td>
<td>No included</td>
</tr>
</tbody>
</table>

Total 99.94 -

The flue gas in the kiln is characterized to be oxidizing. The composition and concentration of the gas used for the thermodynamic calculation of the full system is specified in Table 4-5. The values represent typical values found in the kiln inlet of a cement rotary kiln. All the compounds are inserted in the calculations as mol/kg clinker.

1 The formation of belite starts at temperatures above 700 °C, as it is assumed that part of the silica content is contributed by belite.
Table 4-5: Flue gas composition in oxidizing conditions.

<table>
<thead>
<tr>
<th>Gas composition in oxidizing conditions</th>
<th>Concentration [vol. %]</th>
<th>Concentration [mol/kg clinker]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>25.00</td>
<td>5.580</td>
</tr>
<tr>
<td>O₂</td>
<td>5.00</td>
<td>1.116</td>
</tr>
<tr>
<td>H₂O</td>
<td>5.00</td>
<td>1.116</td>
</tr>
<tr>
<td>SO₂</td>
<td>0.05</td>
<td>0.011</td>
</tr>
<tr>
<td>N₂</td>
<td>64.95</td>
<td>14.49</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>-</td>
</tr>
</tbody>
</table>

The following considerations have been taken for the model:

- A closed co-current system is considered.
- The calculations have been performed assuming one kg calcined raw material and 0.5 Nm³ flue gas for each kg clinker produced.
- The temperature of the calculations is in the range between 900 °C and 1500 °C in a step size of 10 °C and the pressure is 1 atm.
- Ideal gas phase species, solid phase species, and liquid phase species and their physical and chemical properties are included from the software database (Bale et al., 2009). The list of species included in the calculations is specified in Appendix B.

The equilibrium model has the following limitations:

- The model does not consider mass transfer and kinetic limitations. The residence time of the material in the industrial rotary kiln may be too short for the species to transform, decompose or react with each other. Therefore, the predicted formation of species may deviate from reality.
- The model considers pure species and the interaction between the compounds are neglected; just the interactions between the elements of the input compounds are taken into account.
- The data of the software might be not fully reliable at higher range of the temperatures studied, because the C_p data for some of the species listed in Appendix B were out of the temperature ranged.
- The model cannot take into account the uncertainties in the thermodynamic properties.

4.4.1.2 Results and Considerations

Figure 4-21 shows the thermodynamic results of the complex system considering the gas compounds, the main clinker compounds, and compounds containing sulfur, alkali, and chlorine. The concentrations of CO₂ and N₂ in the gas phase are higher than the rest of the species and in order not to shift the magnitude of the y-axis, these species are not presented in the graph.
The abundant solid compounds from 900 to 1300 °C are CaO and dicalcium silicate (belite). At 1300 °C belite starts to not be thermally stable until 1450 °C, where another solid structure of belite is stable. From 1300 to 1500 °C, tricalcium silicate (alite) is the most abundant silicate. The equilibrium concentration of CaO at 1300 °C decreases because calcium is combined with belite to form alite.

In Figure 4-21, Al and Fe are combined as CaAlO₄ (aluminate) and CaFeO₃, respectively. Their equilibrium concentrations do not vary with temperature. However, ferrite (Ca₂Al₂FeO₅), which is one of the clinker minerals, has not been predicted in this calculation. This may be due to the formation of solid aluminate and ferrite from the liquid phase takes place during the cooling, as mentioned in Chapter 2.

The volatile elements are present in the system in minor equilibrium concentrations. Sulfur is found as CaSO₄ and K₂Ca₃(SO₄)₂ at the rotary kiln inlet. Calcium sulfate is the abundant sulfate, which is stable until 1200 °C, where after it starts to decompose until 1320 °C where CaSO₄ is no longer stable. Calcium langbeinite, K₂Ca₃(SO₄)₂, is a double sulfate containing potassium and calcium and is more thermally stable than calcium sulfate. Calcium langbeinite is stable until 1380 °C. At higher temperatures, from 1380 to 1500 °C, the stable sulfate is K₂SO₄ in liquid phase and gas phase. SO₃ in gas phase is released from 1200 °C, when calcium sulfate starts to be less stable. Calcium langbeinite also contributes to higher equilibrium concentration of SO₃ when it is no longer thermally stable. The chlorine compounds in gas phase in the system are KCl, which is the most abundant chloride, and NaCl in the whole range of temperatures studied. From 900 to 930 °C, KCl also appears to be stable in liquid phase.
The results of this complex system do not represent the chemistry of the rotary kiln explained in section 4.1, especially at temperatures higher than 1200 °C. These calculations are assuming perfect mixing between the compounds and local fluctuations are not considered. The equilibrium conditions where local fluctuations take place inside of the rotary kiln, such as nodulization, can be very different from the simulated conditions, which have transport and kinetics limitations. The local fluctuations can also influence the interaction between the volatile compounds and the main clinker phases, for example it has been reported that K and Na can be incorporated in the clinker minerals (Jawed and Skalny, 1977) and this phenomena has not appeared in the thermodynamic simulations.

Due to the complexity of the system and because the focus of the investigation is on the volatile elements, which are in minor concentrations than the clinker elements, the system is simplified to study thermodynamically the effect of the inorganic chemistry consisting of S, K, Na, and Cl.

### 4.4.2 System considering inorganic chemistry

The system model is simplified by only considering the inorganic chemistry and is based on the same composition of hot meal presented in Table 4-3 and the flue gas presented in Table 4-5.

In this section, SiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$ composition is not included. The model does not consider the main clinker chemistry and the interaction with the volatiles species. Therefore, all the volatiles species will be in gas phase in the hot end of the kiln, while in the industrial rotary kiln some of these volatiles will be part of and leave with clinker nodules. So, this model severely overestimates the evaporation of the gas species.

In the next sections, the simplified system model splits apart the different compounds (sulfates and chlorides) in order to study their effect. First, the sulfates are investigated in oxidizing and reducing conditions and then, the effect of chlorides is introduced in the system.

#### 4.4.2.1 Sulfates in Oxidizing Conditions

Based on moles of potassium, sodium, sulfur, and calcium, as elements, in the given composition of the hot meal, the concentration of Na$_2$SO$_4$, K$_2$SO$_4$, CaSO$_4$, and CaO in moles/kg clinker is specified in Table 4-6. It can be seen that the predominant sulfate is CaSO$_4$ with a higher concentration than the alkali sulfates.

<table>
<thead>
<tr>
<th>Hot meal compounds</th>
<th>Concentration [mol/kg clinker]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$SO$_4$</td>
<td>0.032</td>
</tr>
<tr>
<td>K$_2$SO$_4$</td>
<td>0.266</td>
</tr>
<tr>
<td>CaSO$_4$</td>
<td>0.467</td>
</tr>
<tr>
<td>CaO</td>
<td>9.622</td>
</tr>
</tbody>
</table>

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In liquid phase, sodium sulfate appears to be the thermally stable compounds until 1350 °C and potassium chemistry, where CaSO$_4$ does not appear in this results; this may be because the input concentration is quite similar to the K$_2$SO$_4$ input concentration, therefore they are combined as calcium langbeinite. This does not happens when the input concentration of CaSO$_4$ is larger than the input concentration of K$_2$SO$_4$ (see section 4.4.2.3).

Calcium langbeinite, K$_2$Ca(SO$_4$)$_2$ is the most abundant solid sulfate and appears to be thermally stable until 1250 °C and starts to until 1370 C. In solid phase, a double sulfate of potassium and sodium and K$_2$SO$_4$ are also stable in small concentrations, the first one from 900 to 930 °C and the second from 930 to 1060 °C. In In liquid phase, sodium sulfate appears to be the thermally stable compounds until 1350 °C and potassium sulfate from 1060 to 1500 °C with a maximum concentration at 1380°C. The SO$_3$ in the gas phase is mostly produced from the decomposition of the solid sulfates and the concentration also increases above 1370 °C due to the decomposition of alkali sulfates. In the gas phase at temperatures above 1300 °C, there are also in small quantities of K$_2$SO$_4$ and the alkali hydroxides due to the presence of water vapor.

The thermodynamics results are shown in Figure 4-22. Abundant species such as are CaO, CO$_2$, and O$_2$ are not shown in the graph because the presence of these species would shift the magnitude of the y-axis and make impossible to see the behavior of alkali and sulfate containing species.

In In liquid phase, sodium sulfate appears to be stable above 1300 °C while in the solid phase, a double sulfate of potassium and sodium and K$_2$SO$_4$ are also stable in small concentrations, the first one from 900 to 930 °C and the second from 930 to 1060 °C. CaSO$_4$ does not appear in this results; this may be because the input concentration is quite similar to the K$_2$SO$_4$ input concentration, therefore they are combined as calcium langbeinite. This does not happens when the input concentration of CaSO$_4$ is larger than the input concentration of K$_2$SO$_4$ (see section 4.4.2.3).

The behaviors of the solid phases are different as observed in the system considering the inorganic and clinker chemistry, where CaSO$_4$ and K$_2$Ca(SO$_4$)$_2$ appeared to be stable but not KNa(SO$_4$)$_2$ and K$_2$SO$_4$ in Figure 4-21. In liquid phase, Na$_2$SO$_4$ was not predicted in the complex system while in Figure 4-22 is stable in a wide range of temperatures. Furthermore, K$_2$SO$_4$ in liquid phase appeared to be stable above 1300 °C while in the thermodynamic calculations considering only the volatile species is stable from 1060 °C. The gas species 

The thermodynamics results are shown in Figure 4-22. Abundant species such as are CaO, CO$_2$, and O$_2$ are not shown in the graph because the presence of these species would shift the magnitude of the y-axis and make impossible to see the behavior of alkali and sulfate containing species.

In In liquid phase, sodium sulfate appears to be stable above 1300 °C while in the solid phase, a double sulfate of potassium and sodium and K$_2$SO$_4$ are also stable in small concentrations, the first one from 900 to 930 °C and the second from 930 to 1060 °C. CaSO$_4$ does not appear in this results; this may be because the input concentration is quite similar to the K$_2$SO$_4$ input concentration, therefore they are combined as calcium langbeinite. This does not happens when the input concentration of CaSO$_4$ is larger than the input concentration of K$_2$SO$_4$ (see section 4.4.2.3).

In In liquid phase, sodium sulfate appears to be the thermally stable compounds until 1350 °C and potassium sulfate from 1060 to 1500 °C with a maximum concentration at 1380°C. The SO$_3$ in the gas phase is mostly produced from the decomposition of the solid sulfates and the concentration also increases above 1370 °C due to the decomposition of alkali sulfates. In the gas phase at temperatures above 1300 °C, there are also in small quantities of K$_2$SO$_4$ and the alkali hydroxides due to the presence of water vapor.
above 1400 °C are in good agreement with the observation of the system considering the inorganic and clinker chemistry (Figure 4-21).

4.4.2.2 Sulfates in Reducing Conditions

When fuel particles are burned in direct contact with the bed material, the volatiles gases released can react with the hot meal. Therefore, two scenarios will be simulated to calculate the behavior of the hot meal using the flue gas composition in reducing conditions which is shown in Table 4-7.

<table>
<thead>
<tr>
<th>Gas composition reducing cond. 1</th>
<th>Concentration [vol.%]</th>
<th>Gas composition reducing cond. 2</th>
<th>Concentration [mol/kg clinker]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>25.00</td>
<td>CO₂</td>
<td>25.00</td>
</tr>
<tr>
<td>CO</td>
<td>0.10</td>
<td>CH₄</td>
<td>0.10</td>
</tr>
<tr>
<td>H₂O</td>
<td>5.00</td>
<td>H₂O</td>
<td>5.00</td>
</tr>
<tr>
<td>SO₂</td>
<td>0.05</td>
<td>SO₂</td>
<td>0.05</td>
</tr>
<tr>
<td>N₂</td>
<td>69.85</td>
<td>N₂</td>
<td>69.85</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>

The thermodynamics results using the flue gas composition for reducing conditions 1, containing 0.1 vol.% CO, are illustrated in Figure 4-23. The calcium langbeinite equilibrium concentration is lower than in Figure 4-22. Potassium sulfate appears at approx. 1070 °C in liquid phase with maximum equilibrium concentration at 1330 °C (at lower temperature than in Figure 4-22) and from 1380 °C in gas phase. The SO₂ release starts at 900 °C, seems stable until 1100 °C, and increases significantly with temperature from 1200 to 1330 °C, which is produced by the decomposition of the double calcium potassium sulfate, and after by the liquid potassium sulfate. From 1350 until 1500 °C, alkali hydroxides are thermodynamically stable in the gas phase.
Chapter 4: Circulation of Inorganic Elements in the Kiln System

Figure 4-23: Thermodynamic results for the alkali and sulfate species in the temperature of the rotary kiln in reduction conditions 1.

Figure 4-24 shows the thermodynamics results using the flue gas composition for reducing conditions 2, containing 0.1 vol. % CH₄. The results obtained are very similar to the reducing conditions 1. It can be noticed that the SO₂ equilibrium concentration is higher and the calcium potassium sulfate concentration in the kiln inlet of the rotary kiln are lower than for the reducing conditions 1.

Figure 4-24: Thermodynamic results for the alkali and sulfate species in the temperature of the rotary kiln in reduction conditions 2.
In both scenarios, the SO$_2$ and K$_2$Ca(SO$_4$)$_3$ are mainly affected by the reducing atmosphere from 900 to 1200 °C, in the temperature range of the kiln inlet. At the burning zone temperatures 1400-1500 °C, the equilibrium concentrations of the gas species are not affected.

### 4.4.2.3 Effect of Chlorine Addition

The effect of the chlorine species is investigated in this section. Based on moles of potassium, sodium, sulfur, chlorine, and calcium of the hot meal composition in Table 4-3, the concentration of NaCl, KCl, Na$_2$SO$_4$, K$_2$SO$_4$, CaSO$_4$, and CaO in moles/kg clinker is specified in Table 4-8. The flue gas composition in oxidizing conditions is used.

**Table 4-8: Specific concentration of NaCl, KCl, Na$_2$SO$_4$, K$_2$SO$_4$, CaSO$_4$, and CaO in the hot meal.**

<table>
<thead>
<tr>
<th>Hot meal compounds</th>
<th>Concentration [mol/kg clinker]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0.065</td>
</tr>
<tr>
<td>KCl</td>
<td>0.265</td>
</tr>
<tr>
<td>K$_2$SO$_4$</td>
<td>0.133</td>
</tr>
<tr>
<td>Na$_2$SO$_4$</td>
<td>0.000</td>
</tr>
<tr>
<td>CaSO$_4$</td>
<td>0.632</td>
</tr>
<tr>
<td>CaO</td>
<td>9.496</td>
</tr>
</tbody>
</table>

The thermodynamic results with the effect of chlorine are shown in Figure 4-25. The behaviors of the sulfates and chlorides are quite similar to the observed behavior in the system considering inorganic chemistry with clinker chemistry. KCl is mainly thermodynamic stable in the gas phase, liquid phase between 900 to 930 °C, and a dimer of KCl in the gas phase is also thermally stable in the material kiln inlet. This was also observed in the thermodynamic results of the complex system. CaSO$_4$ and the double calcium potassium sulfate are found to be thermodynamically stable until 1200 and 1350 °C, respectively. The SO$_2$ is mainly caused by the decomposition of CaSO$_4$ and after of K$_2$Ca(SO$_4$)$_3$. There are no sulfates in liquid phase as observed in Figure 4-22, Figure 4-23 and Figure 4-24. At temperatures corresponding to the burning zone, from 1350 °C, potassium sulfate and alkali hydroxides in gas phase appear stable and this has also been observed in the previous graphs.

Chapter 4: Circulation of Inorganic Elements in the Kiln System
Through the thermodynamic software, the presence of sodium species, such as NaOH and Na$_2$SO$_4$ in gas phase has been observed. However, the concentrations are in the order of $10^{-2}$ mol/kg clinker, or lower, and can therefore not be noticed in Figure 4-25.

4.4.2.4 Effect of Higher Concentration of Alkali than Sulfur

The effect of higher concentration of alkali than sulfur is investigated in this section. A hypothetical composition of the hot meal is specified in Table 4-9. This composition would also contain MnO$_2$, TiO$_2$, SrO, MgO and P$_2$O$_5$ but are not considered in the calculations and therefore not specified. It needs to be noticed that this composition may not be realistic, because it is not desired to have excess of alkali content in the clinker due to its negative effect on the cement mechanical properties. This hot meal is exposed to the flue gas in oxidizing conditions.
Chapter 4: Circulation of Inorganic Elements in the Kiln System

The results of the thermodynamic calculation for this system are shown in Figure 4-26. It should be noticed that the y-axis scale of this figure is different from the previous graphs in this section. The SO₄ concentration is much lower than in the previous calculation. Calcium sulfate is not present in the system, instead calcium sulfate is bound with alkali as calcium langbeinite, K₂Ca₃(SO₄)₃(OH), which is stable until 1300 °C. Double alkali sulfate, K₃Na₂(SO₄)₄ is stable at the inlet of the rotary kiln. Sodium and potassium sulfate are mainly thermodynamic stable in liquid phase, from 900 to 1200 °C and thereafter their equilibrium concentrations decrease. In the burning zone, potassium hydroxide is the main alkali gas species, followed by potassium sulfate and sodium hydroxide, which are stable in low concentrations.

Table 4-9: Hypothetical composition of hot meal used in the equilibrium calculations in section 4.4.2.4, when the concentration of alkali is higher than the sulfur concentration. This composition would also contain MgO, TiO₂, SrO, MgO and P₂O₅, but are not considered in the calculations and therefore not specified.

<table>
<thead>
<tr>
<th>Hot meal composition</th>
<th>Concentration [wt. %]</th>
<th>[mol/kg clinker]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>18.00</td>
<td>3.000</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.76</td>
<td>0.467</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.30</td>
<td>0.144</td>
</tr>
<tr>
<td>CaO</td>
<td>56.80</td>
<td>10.128</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.23</td>
<td>0.240</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.67</td>
<td>0.269</td>
</tr>
<tr>
<td>SO₃</td>
<td>3.4</td>
<td>0.425</td>
</tr>
<tr>
<td>Cl</td>
<td>1.17</td>
<td>0.330</td>
</tr>
</tbody>
</table>

Based on moles of K, Na, S, and Ca from the hypothetical composition of hot meal, the Na₂SO₄, K₂SO₄, CaSO₄, and CaO concentrations in mol/kg clinker are specified in Table 4-10.

Table 4-10: Specific concentration of Na₂SO₄, K₂SO₄, CaSO₄, and CaO in the hot meal.

<table>
<thead>
<tr>
<th>Hot meal compounds</th>
<th>Concentration [mol/kg clinker]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂SO₄</td>
<td>0.269</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>0.240</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>0.000</td>
</tr>
<tr>
<td>CaO</td>
<td>10.128</td>
</tr>
</tbody>
</table>

The results of the thermodynamic calculation for this system are shown in Figure 4-26. It should be noticed that the y-axis scale of this figure is different from the previous graphs in this section. The SO₄ concentration is much lower than in the previous calculations. Calcium sulfate is not present in the system, instead calcium sulfate is bound with alkali as calcium langbeinite, K₂Ca₃(SO₄)₃(OH), which is stable until 1300 °C. Double alkali sulfate, K₃Na₂(SO₄)₄ is stable at the inlet of the rotary kiln. Sodium and potassium sulfate are mainly thermodynamic stable in liquid phase, from 900 to 1200 °C and thereafter their equilibrium concentrations decrease. In the burning zone, potassium hydroxide is the main alkali gas species, followed by potassium sulfate and sodium hydroxide, which are stable in low concentrations.

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<table>
<thead>
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<th>Concentration [wt. %]</th>
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<tr>
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<tr>
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<td>0.425</td>
</tr>
<tr>
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<td>1.17</td>
<td>0.330</td>
</tr>
</tbody>
</table>

Based on moles of K, Na, S, and Ca from the hypothetical composition of hot meal, the Na₂SO₄, K₂SO₄, CaSO₄, and CaO concentrations in mol/kg clinker are specified in Table 4-10.

Table 4-10: Specific concentration of Na₂SO₄, K₂SO₄, CaSO₄, and CaO in the hot meal.

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<thead>
<tr>
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<tr>
<td>Na₂SO₄</td>
<td>0.269</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>0.240</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>0.000</td>
</tr>
<tr>
<td>CaO</td>
<td>10.128</td>
</tr>
</tbody>
</table>
The inorganic chemistry is significantly changed when higher alkali concentrations than sulfur are present in the system. Even though an acceptable clinker quality might be obtained, the liquid phases may disturb the operation process by, for example, rings in the kiln. The SO$_2$ concentration in the gas phase is lower than in previous cases, but there is a higher concentrations of alkali species in the gas phase, which may cause operational problems. For that reason, a balance between sulfur and alkalis is needed in order to avoid high amounts of volatiles species.

### 4.4.3 Concluding Remarks about Thermodynamic Equilibrium Calculations

Comparing the thermodynamics results and the behavior of the circulation of volatiles explained in section 4.1, it can be seen that the behavior of the system including sulfates and chlorides (Figure 4.25) is in a good agreement with the reaction affinity between the volatiles elements (section 4.1.1) and with the description of stability of the sulfates in the kiln inlet of the rotary kiln. However, the thermodynamic calculations do not simulate the behavior of the sulfate species in the transition and hot zone of the kiln. The sulfate melt is not predicted in the calculations and the concentrations in the gas species are overestimated because these species are not retained in the solid phase (clinker). The deviations may be due to the model limitations about perfect mixing, mass transfer and kinetics.

Under reducing atmospheres, the thermodynamics results showed that the stability of sulfates in the inlet of the rotary kiln is strongly affected by the gas atmosphere and become more sensitive. The reducing gas also...
affects to the stability of $\text{SO}_4$, which starts to be stable already at 900 °C. Therefore, the reducing conditions in the kiln inlet will be the focus of this thesis in the following chapters.

The volatility of the chlorine is not affected by the gas atmosphere, but is very sensitive to the temperature. Higher levels of alkali compared sulfur reduces the sulfur release in gas phase, but increases the liquid formation in the kiln and the alkali species in the gas phase. This might lead to unacceptable clinker quality and an increase of volatile compounds in the gas phase which could probably cause an increase of blockages when these species condense in cooler part of the kiln system.

4.5 Conclusions

Volatiles elements, such S, Cl, K, and Na, form a high degree of internal circulation in the rotary kiln, calciner and preheater, by repetitive evaporation and condensation at different temperatures. The volatilization of sulfur depends on the alkali-sulfur ratio, and on the operating conditions, while the volatilization of Cl depends only on the burning zone temperature. The high internal circulation of S and Cl may cause formation of build-ups in the lower cyclones and the riser pipe. In order to avoid this tendency, the hot meal content of $\text{SO}_4$ should be maintained below 6 wt. %, and the Cl content below 2 wt. %.

The process stability of the kiln system can be affected by introduction or an increase of the elements involved in the cement chemistry, reducing conditions, increase in the circulation phenomena in the kiln system, build-ups formation and shell corrosion.

The sulfur and chlorine circulation may increase when alternative fuels are combusted. Sulfur circulation is provoked by the reducing agents released during the combustion of alternative fuels. Coatings from different cement plants have been characterized analytically. Spurrite and KCl have been found to be responsible for the tendency of build-ups and the crystallization of KCl has been postulated to take place by a vapor-liquid-solid mechanism. The risk of formation of buildups can be evaluated by the sulfur and chlorine content in the raw meal.

The high concentrations of SO$_4$ and HCl in presence of moisture makes the kiln gas very corrosive atmosphere and can lead to corrosion of rotary kiln shells and calciner shells.

The thermodynamic calculations have further investigated the inorganic chemistry of sulfur, chlorine, and alkali compounds. In a system containing sulfur, chlorine and alkalis, the stability of the sulfate species in the kiln inlet is in good agreement with the real behavior observed in the cement plants. The reducing agents in the gas phase affect significantly the stability of CaSO$_4$ and SO$_4$ in the kiln inlet, which decreases for CaSO$_4$ and increases for SO$_4$ already at temperatures between 900 to 1100 °C. Thereby the focus of the following chapters will be on the effect of reducing conditions on calcium sulfate in the kiln inlet.
4.6 References

Chapter 4: Circulation of Inorganic Elements in the Kiln System

References
Chapter 4: Circulation of Inorganic Elements in the Kiln System


Chapter 4: Circulation of Inorganic Elements in the Kiln System


Jensen, L.K.; Personal communication about high temperature splits in the calciners, August 27, 2014.


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Karlsson, A., Personal communication about an acceptable level corrosion rate in kiln shell, November 22, 2013.


Jons, E.; Managing volatile components in kiln and preheater, IPSC lecture nr: 05-02. The International Cement Production Seminar. FLSmidth Institute; Valby, Denmark, 2013.


Karlsson, A., Personal communication about an acceptable level corrosion rate in kiln shell, November 22, 2013.


82


Chapter 4: Circulation of Inorganic Elements in the Kiln System


Rahman, H., and Krakpat, T.; Discussion about "Ideally the value alkali to sulphate ratio should be as close to 1 as possible, i.e. the alkali and sulphate should be in molar balance" in Cement Industry Expert group in www.linkedin.com, 2012. Accessed in 10/3/2013.


Smith, L.; Volatile matter, IPSC lecture nr: 05-02. The International Cement Production Seminar. FLSmidth Institute, Valby, Denmark, 2012.


5. Sulfur Release during Combustion of Alternative Fuels Particles

This chapter seeks to extend the knowledge of the sulfur release from hot meal during combustion of solid alternative fuel particles in the kiln inlet of a rotary kiln.

Section 5.1 covers the literature study about the sulfur release during combustion of solid fuels, which will be the starting point for the experimental investigations. The experimental part, section 5.2, describes the pilot scale equipment used for simulating the process conditions at the material inlet end of industrial rotary kilns. The solid fuels used for the experiments, tire derived fuels and wood, and their preparation are also introduced in the experimental section. Section 5.3 presents a parametric study of the effect on the release of sulfur; parameters such as particle size of different fuel types, fuel conversion degree, sulfur load in the bed and moisture content of the fuel are modified.

5.1 Literature Study on Sulfur Release in the Kiln System

5.1.1 Phase Diagrams for CaSO$_4$-CaO-CaS system

The high temperature reactions of SO$_2$ absorption and release under fluidized bed and entrained flow conditions have been studied extensively (Dam-Johansen and Østergaard, 1991a; Dam-Johansen and Østergaard, 1991b; Hansen et al., 1993; Lyngfelt and Eckner, 1993; Barletta et al., 2002). However, these investigations cannot be used directly to describe the conditions at the kiln inlet, because the Ca/S molar ratio studied under fluidized bed conditions were typically in the rage of 1:1 to 4:1, which differs from the conditions in cement rotary kilns where Ca/S molar ratio is typically higher than 10:1 (Hewlett, 1998). The descriptions of the mechanism for sulfur release and capture will be discussed further in Chapter 6.

In Hansen’s investigations, it was proposed that in a system consisting of CaSO$_4$, CaO, CaS, SO$_2$, CO, and CO$_2$, sulfur is captured as CaSO$_4$ under oxidizing conditions, and as CaS under reducing conditions, i.e. in the presence of CO (Hansen et al., 1993). Any transformation of CaSO$_4$ to CaS and vice versa appears to proceed via CaO, as illustrated in Figure 5-1. Equilibrium phase diagrams for this system show that the transformation cycle depends on the partial pressures of SO$_2$, CO and CO$_2$ and the temperature (Hansen et al., 1993), as illustrated in Figure 5-2.
Figure 5-2 shows three regions, corresponding to the stability of CaSO_4, CaO and CaS. Moving from left to right in this figure indicates a shift from oxidizing to reducing conditions. It is seen that CaSO_4 is stable under oxidizing conditions, whereas CaS is stable at higher reducing potentials. An increase in temperature rapidly shifts the phase limits upwards, where the stability regions of CaSO_4 and CaS decreases and the stability region of CaO increases. For low SO_2 partial pressures, the transition from CaSO_4 to CaS passes through CaO and this transition is favored by increasing temperature. However, this contradicts Figure 5-1 and the mechanism of sulfur release and capture proposed by Hansen et al. (1993).

Similar phase diagrams for the equilibrium system consisting of CaSO_4, CaO, CaS, SO_2, H_2, and H_2O are shown in Figure 5-3 and Figure 5-4. The H_2O partial pressures are 0.6 and 0.2 atm, respectively. The effect of temperature on the stability regions is similar to the observed effect on the CaSO_4, CaO, CaS, SO_2, CO, and CO_2 system. Increasing the H_2O partial pressure (the moisture content in the system), the stability region for CaSO_4 is increased and therefore favoring the oxidizing conditions.
Chapter 5: Sulfur Release during Combustion of Alternative Fuels Particles

Figure 5-3: Phase diagram for the SO\textsubscript{2}-CaO-CaSO\textsubscript{4}-CaS-H\textsubscript{2}O system at 800, 900, 1000, 1100 and 1200 °C. Total pressure 1 atm and 6 vol. % H\textsubscript{2}O giving P\textsubscript{H\textsubscript{2}O}=0.06 atm (thermodynamic data from Barin, 1995).

Phase diagram for the system containing CaSO\textsubscript{4}, CaO, CaS, and SO\textsubscript{2} as function of the partial pressure of O\textsubscript{2} in the temperature range 800 to 1200 °C is illustrated Figure 5-5. The phase diagram shows that the CaSO\textsubscript{4} stability decreases with decreasing partial pressure of oxygen, passing to CaS or CaO, depending on the partial pressure of SO\textsubscript{2} and the temperature (Hansen et al., 1993).

5.1.2 Sulfur Release during Combustion of Solid Fuels

Sulfur release from the cement raw materials during combustion of solid fuels has been studied scarcely. Nielsen (2012) studied sulfur release from model raw materials consisting of a mixture of CaSO\textsubscript{4} and quartz sand in a rotary drum in the temperature range between 700 to 1000 °C. The alternative fuels used were...
polypropylene, petcoke, wood, saw dust, tire, and sewage sludge. Table 5-1 specifies the fuel analysis, where a.r. denotes as received, and the lower heating values, and Table 5-2, their shape and dimensions. The effects of energy input, fuel type, temperature, and bulk oxygen concentration were studied.

The sulfur release was corrected by subtracting the sulfur release coming from the fuel sulfur content and from the thermal decomposition of the calcium sulfate. Figure 5-6 shows the total sulfur release as a function of the energy input from different fuels at 900 °C. Increasing energy input led to a higher degree of reducing conditions near the raw materials bed and more sulfur was therefore released. Figure 5-7 shows the results of the sulfur release from raw materials in the temperature range 700 to 1000 °C for different fuels with different dimensions, specified in Table 5-2. The uncertainties of the results have been added in both graphs. The relative uncertainty of the experimental data in Figure 5-6 is greater when using high energy input, i.e. for the experiments using 15 kJ, the relative uncertainty varies between 10 to 19 %, and 27 to 42 % using 50 kJ.

Table 5-1: Fuel analyses and lower heating values (LHV) for solid fuels used in the experiments of used in Figure 5-6, Figure 5-7, and Figure 5-8.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Proximate analysis [wt. %]</th>
<th>Ultimate analysis [wt. %]</th>
<th>LHV [MJ/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>VM</td>
<td>FC</td>
<td>Ash</td>
</tr>
<tr>
<td>Tire rubber granulate</td>
<td>64.6</td>
<td>32.6</td>
<td>2.8</td>
</tr>
<tr>
<td>Tire rubber cylinders</td>
<td>75.3</td>
<td>24.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Pine wood</td>
<td>97.5</td>
<td>0.0</td>
<td>2.5</td>
</tr>
<tr>
<td>Poly propylene</td>
<td>13.4</td>
<td>85.1</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 5-2: Approximate shapes and dimensions of the fuels used in Figure 5-6, Figure 5-7, and Figure 5-8 (Nielsen, 2012). Length (L) and diameter (ø).

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Shape</th>
<th>Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tire rubber granulate</td>
<td>Irregular</td>
<td>ø ≈ 2 mm</td>
</tr>
<tr>
<td>Tire rubber cylinders</td>
<td>Cylindrical</td>
<td>L = 12 mm, ø = 9 mm</td>
</tr>
<tr>
<td>Pine wood cubes</td>
<td>Rectangular</td>
<td>20x15x10 mm</td>
</tr>
<tr>
<td>Pine wood saw dust</td>
<td>Needles</td>
<td>L = 1 mm</td>
</tr>
<tr>
<td>Poly propylene flakes</td>
<td>Rectangular</td>
<td>20x30x1 mm</td>
</tr>
<tr>
<td>Petcoke</td>
<td>Spherical</td>
<td>ø ≈ 1 mm</td>
</tr>
<tr>
<td>Sewage sludge granulate</td>
<td>Spherical</td>
<td>ø ≈ 0.5 mm</td>
</tr>
</tbody>
</table>

The sulfur release was corrected by subtracting the sulfur release coming from the fuel sulfur content and from the thermal decomposition of the calcium sulfate. Figure 5-6 shows the total sulfur release as a function of the energy input from different fuels at 900 °C. Increasing energy input led to a higher degree of reducing conditions near the raw materials bed and more sulfur was therefore released. Figure 5-7 shows the results of the sulfur release from raw materials in the temperature range 700 to 1000 °C for different fuels with different dimensions, specified in Table 5-2. The uncertainties of the results have been added in both graphs. The relative uncertainty of the experimental data in Figure 5-6 is greater when using high energy input, i.e. for the experiments using 15 kJ, the relative uncertainty varies between 10 to 19 %, and 27 to 42 % using 50 kJ.
The fuel particle size had an insignificant influence on sulfur release at 700 and 800 °C, where there were almost no sulfur release for any fuels. The influence of particle size became more evident at 900 and 1000 °C for the different fuels. Comparing the tire rubber and wood particles, the tire granulate and saw dust gave rise to higher sulfur release while the sulfur release was much less for the tire and wood particles. The sulfur releases from the tire granulate and the saw dust in Figure 5-7, was estimated by extrapolation since the SO₂ concentration exceeded the range of the analyzer. The relative uncertainty of the results at different temperatures is normally higher at 700 °C and lower at 1000 °C, but does not follow any trend and varies from 3 to 83 %.

The effect of oxygen concentration on sulfur release is shown in Figure 5-8. The total sulfur release increased with decreasing oxygen concentration. This is in a good agreement with the phase diagram of Figure 5-5, because CaSO₄ is more stable at higher O₂ concentrations and will need stronger reducing conditions to be transformed to CaS and/or CaO. The relative uncertainties are greatest at 5 and 10 vol. % O₂, which are around 20 % for tire granulate and polypropylene, and 72 and 51 %, for pet coke and wood at 10 vol. % O₂, respectively. This may be due to incomplete combustion, creating significant amount of soot, and how the particles were mixed with the bed, which could have been very different from experiment to experiment. At higher O₂ content, the relative uncertainties are 10 % or below.

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5.1.2.1 Pre-experimental Considerations

In previous experiments, it has been observed that the fuel particle size is of high importance for the sulfur release, but it is not clear why. Further experiments with different particle sizes will be done in order to clarify whether this is due to fuel composition, the conversion pathway, or the number of particles.

Furthermore, the effect of fuel devolatilization degree would represent the sulfur release of partly unburned alternative fuel and give an idea of the sulfur release from calcined raw meal when partly unburned solid alternative fuels from the calciner fall into the kiln inlet directly or after being carried upwards with the gas flow in the calciner and transported into the bottom stage cyclone to the kiln inlet. It is well known that the reducing gases such as CO, H\textsubscript{2}, and CH\textsubscript{4}, which can be released from the fuel particle, cause reductive decomposition of CaSO\textsubscript{4} (Swift and Wheelock, 1975; Wheelock and Boylan, 1960; Oh and Wheelock, 1990; Nielsen, 2012) but the effect of the fuel char or partly converted fuel has been not investigated in the literature.

In all the experiments performed by Nielsen (2012), the alternative fuel was dried. In reality, most of the alternative fuels contain a high degree of moisture, which could affect the sulfur release, and this will also be investigated in section 5.3.

Nielsen (2012) did not use cement raw materials based on clay and limestone because it adhered to the rotary drum inner walls and formed nodules during the experiments. In addition, the raw meal did not roll in the drum but moved in a slumping motion. It has been noticed that the uncertainties of Nielsen’s experiments are large. The used quartz sand had a particle size range between 0.4 to 1 mm with average size of 0.6 mm (Nielsen, 2012). The actual particle size distribution of the quartz sand is shown in Figure 5-9. Pre-experiments were...
done to improve the repeatability. Differences in the distribution of the quartz particles in the experimental setup prior to and after an experimental series were noticed. Prior to experiments the particles were homogenously distributed in the setup whereas after experiments the smaller particles were placed on the sides of the reactor and the bigger particles in the middle.

Figure 5-9: Particle size distribution for the quartz sand.

The particle size distribution of the quartz sand clearly affected the calcium sulfate added in the mixture because it was moving in the axial direction, which means that the sulfur content was not homogeneous along the bed. Therefore, it was decided to narrow the particle size distribution of the quartz sand, which improved the experimental repeatability significantly from 16-28 % to 1-5 % in relative uncertainty. Quartz sand with a particle size range from 0.4 to 0.8 mm are used in the experiments of this thesis.

5.2 Experimental

The aim of the experimental section is to investigate the effect of particle size of different fuels, degree of fuel devolatilization, sulfur content in the bed, and moisture content on release of sulfur from cement raw materials.

5.2.1 Experimental Set-up

The experiments are performed in a high temperature rotary drum (Nielsen, 2012). This equipment is able to simulate the process conditions at the material inlet end of an industrial rotary kiln. The rotary drum is electrically heated by a furnace. Gas can be introduced into the chamber furnace through a hole in the roof in order to have a controlled atmosphere. The gas is transported into the rotating drum by an externally placed gas pump that pumps the gas through the rotating drum and the steel tube where after the gas exiting the reactor

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is cooled and analyzed. The exit concentrations of SO\textsubscript{2}, CO, CO\textsubscript{2}, and O\textsubscript{2} in the gas are analyzed and logged during the fuel combustion. The chamber furnace door is equipped with a window for visual inspection, two holes for thermocouples, and a centrally placed water cooled tube for introduction of solid fuel. The solid fuels are placed in a sample container which can be pushed into the hot rotary drum or pulled out to the water cooled tube. Figure 5-10 shows a side and top view of the high temperature rotary drum and its dimensions in mm.

Figure 5-10: High temperature rotary drum. Left: Side view. Right: Top view (Nielsen, 2012). Note: T1, T2 and T3 refer to thermocouples, L refers to length and ø to diameter in mm.

Figure 5-11 shows the piping and instrumentation diagram of the high temperature rotary drum. The nitrogen and air can be sent into the furnace but can also be bypassed during calibration of flow meter controllers and leakage tests. The gas temperature is measured at three different positions in the rotary drum reactor: at the rear wall in the chamber furnace (T1), which is regulated by a Programmable Logic Controller (PLC), at the center of the rotary drum (T2) and at the door just in front of the rotary drum (T3). The rotation of the rotary drum is regulated by a speed controller (S1), which controls the motor (M1).

Figure 5-11: P&I diagram of the high temperature rotary drum (Nielsen, 2012).
A pump transports the flue gas out of the rotary drum reactor. Before passing the pump, the flue gas is cooled in a heat exchanger and soot particles are captured in a filter. After having passed the pump, the flue gas is either sent directly to the stack, or to the gas analyzers for measurement of O\(_2\), CO, CO\(_2\), SO\(_2\), and NO. The fraction of the flue gas which is sent to the analyzers will pass additional two filters, a gas cooler for condensation of water and a sample gas pump before reaching the gas analyzers. IR analyzers are used for CO and CO\(_2\), an UV analyzer is used for NO and SO\(_2\), and a paramagnetic analyzer is used for O\(_2\).

The operational limits of the experimental set-up are described in Table 5-3.

### Table 5-3: Key specifications for high temperature drum experimental setup (Nielsen, 2012)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating temperature</td>
<td>( \leq 1000^\circ C )</td>
</tr>
<tr>
<td>Rotational speed</td>
<td>0-20 rpm</td>
</tr>
<tr>
<td>Gas flow</td>
<td>( \leq 500 \text{ NL/min} )</td>
</tr>
<tr>
<td>Oxygen concentration</td>
<td>2-21 vol. %</td>
</tr>
<tr>
<td>Load capacity</td>
<td>( \leq 6 \text{ L} )</td>
</tr>
<tr>
<td>Fill degree</td>
<td>( \leq 17 % )</td>
</tr>
</tbody>
</table>

#### 5.2.2 Experimental Method

As stated in the pre-experimental considerations, a model mixture of raw materials is used in the experiments of this project. The mixture is based on inert quartz sand with a particle size ranging from 0.5 to 0.71 mm, and CaSO\(_4\) as source of sulfur.

The synthetic mixture is placed in the rotary drum in the desired volumetric filling degree, typically 5 %. The furnace door is closed and the reactor heated to the desired temperature. The drum is rotating with 6 rotations per minute, which keeps the raw materials in a rolling motion with an angle of repose of approximately 30-40\(^\circ\). A constant flow of 100 NL/min of gas with the desired O\(_2\) concentration in N\(_2\) is sent through the rotary drum.

At a desired temperature, controlled by T2, and oxygen concentration monitored by the gas analyzer, the fuel sample is placed in the sample boat, which is then positioned in the water cooled tube. The water cooled tube is closed in the end, in order to obtain a controlled atmosphere inside the rotary drum reactor. When the temperature measured by T2 and oxygen concentration are stable inside the reactor, the fuel sample boat is pushed into the rotary drum, turned 180\(^\circ\) and pulled out in the water cooled tube again. Thereby, the fuel sample will drop on the synthetic bed material and immediately be heated and start combustion.
The filters in the experimental set-up are changed regularly in order to avoid significant pressure drop over the system because this creates an unstable gas flow, which will affect the repeatability of the individual experiments.

The release of sulfur during the experiments is quantified by integration of the gas concentration of SO₂ over the relevant time interval, which mathematically is expressed by equation 5.1. The SO₂ release during thermal decomposition of CaSO₄ (when no experiments are conducted) must be subtracted from the actual measurements in order to quantify only the release caused by the fuel combustion.

\[ n_{\text{release}} = \int \frac{y_{\text{SO}_2} \, dq}{R \cdot T} \cdot P \cdot Q \, dt \quad [5.1] \]

where \( y_{\text{SO}_2} \) is the SO₂ concentration in ppm, \( R \) the gas ideal constant (8.314 m³·Pa/mol·K), \( P \) the atmospheric pressure in Pa, \( T \) the temperature in K, and \( Q \) the volumetric gas flow in m³/s.

Assuming that the fuel conversion is proportional to the carbon conversion, the degree of fuel conversion, \( X \), can be calculated by integration of the concentrations profiles of CO₂ and CO (\( y_{\text{CO}_2} \) and \( y_{\text{CO}} \)), as described by equation 5.2.

\[ X(t) = \frac{\int y_{\text{CO}_2} \, dq + y_{\text{CO}} \, dt}{\int y_{\text{CO}_2} \, dq + y_{\text{CO}} \, dt} \quad [5.2] \]

5.2.3 Fuel Samples

Pine wood and tire rubber cylinders are used as fuels. Their proximate and ultimate analyses as received and the lower heating values are shown in Table 5-4.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Moisture [wt. %]</th>
<th>Proximate analysis [wt. %]</th>
<th>Ultimate analysis [wt. %]</th>
<th>LHV [MJ/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>VM₆</td>
<td>FC</td>
<td>Ash</td>
</tr>
<tr>
<td>Pine Wood</td>
<td>11.4</td>
<td>76.8</td>
<td>11.3</td>
<td>0.5</td>
</tr>
<tr>
<td>Tire rubber</td>
<td>-</td>
<td>64.4</td>
<td>32.6</td>
<td>2.8</td>
</tr>
</tbody>
</table>
Three types of particle size of pine wood and tire rubber are chosen in order to investigate the effect of particle size. The cylinder dimensions of pine wood and tire rubber are specified in Table 5-5. It was not possible to use identical dimensions of wood and tire cylinders due to the high energy input of tire.

Table 5-5: Cylinders dimensions of pine wood and tire rubber. Length (L) and diameter (ø). Note: * Granulate.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Particle size [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pine wood</td>
<td>ø=19 , L= 25</td>
</tr>
<tr>
<td></td>
<td>ø=13 , L=25</td>
</tr>
<tr>
<td></td>
<td>ø=8 , L=12</td>
</tr>
<tr>
<td>Tire rubber</td>
<td>ø=13 , L=12</td>
</tr>
<tr>
<td></td>
<td>ø=9 , L=12</td>
</tr>
<tr>
<td></td>
<td>ø=2*</td>
</tr>
</tbody>
</table>

5.2.4 Wood Char Preparation

The wood char is made by introducing the wood cylinders into a horizontal tube reactor under a nitrogen atmosphere for 20 minutes at a specific temperature. The horizontal tube reactor is an Entech two-zone electrically heated furnace consisting of a ceramic pipe, which is heated by three electrical heaters, and water cooled flanges at both ends. The length of the ceramic pipe is 1150 mm and the inner and outer diameters are 50 and 60 mm, respectively. The reactor has also a gas panel, which allows using the desired gas and flow. The outlet gas can be filtrated and analyzed or send it directly to ventilation. Figure 5-12 shows a schematic view of the different parts of the horizontal tube reactor.

The wood cylinders are placed in a porcelain crucible with dimensions of HxWxL=17x35x90 cm. The porcelain crucible is placed in the water cooled chamber, which makes it possible to remove and insert the wood cylinder while the oven is hot and while maintaining the gas composition. For all the wood char preparation, a minimum time of 5 minutes after sealing of the oven is kept to ensure that no oxygen is inside the system after the pipe has been open. The sealing is done with a stainless steel plate which contains an opening for the gas inlet. The crucible is pushed into the center of the ceramic tube using a metal stick. After 20 minutes, the crucible is pushed fast to the water cooled chamber with a metal tube from the back end in order to minimize the entrance of oxygen into the reactor. In the water cooled chamber the crucible and the samples are cooled down in nitrogen during 10 minutes.
Wood char is produced at temperatures of 300, 500, 700 and 900 °C with a constant N₂ flow of 5 NL/min in all the experiments. The used nitrogen has a purity of 99.999%. The mass before and after the pyrolysis of each cylinder are measured. It should be noticed that the cylinders shrunk during pyrolysis. Table 5-6 shows the average dimensions of the wood cylinders after the pyrolysis at different temperatures. The degree of devolatilization for the three different wood cylinders and the average at different temperatures are also specified in Table 5-6.

Table 5-6: Average dimensions and degree of devolatilization for the wood cylinders after the 20 min of pyrolysis at different temperatures. Length (L) and diameter (ø). Note: Average, °Degree of devolatilization above 100%, which means that the particle does not contain volatiles and have experienced char degradation.

<table>
<thead>
<tr>
<th>T [°C]</th>
<th>Particle size after pyrolysis [mm]</th>
<th>Degree of devolatilization [%]</th>
<th>Avg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>ø 7, L= 24</td>
<td>ø 11-12, L= 24</td>
<td>ø 17-18, L= 24</td>
</tr>
<tr>
<td>500</td>
<td>ø 5-6, L= 21</td>
<td>ø 8-9, L= 21</td>
<td>ø 12-14, L= 22</td>
</tr>
<tr>
<td>700</td>
<td>ø 4-5, L= 20</td>
<td>ø 8-9, L= 20</td>
<td>ø 12-10, L= 21</td>
</tr>
<tr>
<td>900</td>
<td>ø 4-6, L= 20</td>
<td>ø 9, L= 20</td>
<td>ø 10-12, L= 20</td>
</tr>
</tbody>
</table>

The degree of devolatilization is calculated on basis of the content of volatiles before and after pyrolysis. The analysis of the volatiles content of the non-pyrolyzed wood was determined at 900 °C during 7 minutes (FLSmidth A/S, 2007). It can be seen that the degree of devolatilization for the wood particles at 700 and 900 °C are above 100%, which naturally does not have physical meaning. These numbers occur because the release of volatiles has been completed and decomposition of the char residue starts to occur due to the increased pyrolysis temperature (Koutsoyannopoulos et al., 1989; Di Blasi, 2009). The degree of devolatilization of the three different diameters at the same temperature differ slightly due to the internal heat transfer limitations where internal temperature gradients in the fuel particle occur during heating. The boundary between internal and external heat transfer limitations is defined by the Biott number (Bi), which depends on the thermal conductivity and particle size of the fuel. For the particle sizes used, the internal heating rate is more important than the external heating rate (Bi = 0.2).

5.3 Results and Discussion

5.3.1 General Observations

Figure 5-13 and Figure 5-14 show an example of the flue gas concentrations (O₂, CO, CO₂ and SO₂) from a typical experiment with combustion of a single wood cylinder with a diameter of 19 mm performed at 900 °C and 5 vol. % O₂ and a bed material of 5 % fill degree with 2 wt. % CaSO₄. When the devolatilization starts, the oxygen concentrations drops to approximately 2 vol. % and the CO and CO₂ concentrations increases. The...
SO\(_2\) concentration increases rapidly from 0 to almost 300 ppm and gradually decreases towards 0 ppm again while the CO\(_2\) concentration also decreases.

The normalized carbon conversion curve for the wood cylinder of 19 mm diameter is shown in Figure 5-15 from which the devolatilization and char oxidation times can be determined as indicated. The devolatilization period ends when the slope of the conversion curve decreases significantly, indicating the start of the slower char oxidation period. The char oxidation is assumed to be finished when the CO\(_2\) concentration reaches the same value as the CO\(_2\) concentration in 5 vol. % O\(_2\) in the mixture nitrogen and air, which is 0.03 vol. % CO\(_2\). This assumption is in good agreement with the visual observations during the experiment where red-glowing char particles can be observed in the bed until the CO\(_2\) concentration reaches values below 0.03 vol. % CO\(_2\).
5.3.2 Effect of Particle Size of Different Fuel Types

The influence of particle size on sulfur release from the synthetic raw materials at conditions corresponding to the kiln inlet is illustrated in Figure 5-16 and in Figure 5-17, respectively for tire rubber and pine wood. The experiments are performed in a quartz sand bed of 5 % fill degree with 2 wt. % CaSO$_4$ at 900 °C and oxygen concentrations of 5 and 10 vol. % in N$_2$. All experiments use an identical energy input of 55 kJ in order to compare the effect of particle size. This means the mass of the wood cylinders and the mass of tire rubber are kept constant, therefore 5 cylinders of 8 mm diameter, 2 cylinders of 13 mm diameter and 1 cylinder of 19 mm are used, while for the tire rubber, a single cylinder of 13 mm diameter, and two cylinders of 9 mm diameter are used. It was not possible to use identical dimensions of wood and tire cylinders due to the high energy input of tire.

When combusting tire particles, sulfur is emitted due to the chemical composition of the particles. The sulfur emission originating from the tire particles is quantified by measuring the SO$_2$ release in a bed consisting of quartz sand without CaSO$_4$, and the displayed figure shows the corrected SO$_2$ release from the simulated raw materials after subtraction of the SO$_2$ release from the fuels.
For all particles sizes and both fuels, the SO$_2$ release decreases with increasing oxygen concentration. This effect is also observed by Nielsen (2012) but current results have a better repeatability, an average relative uncertainty of 22 versus 3%. The high concentration of oxygen in the freeboard atmosphere may react with the reducing agent and thereby lower the concentration of the reducing agent, which react with CaSO$_4$. Another possibility is that the oxygen may influence the reductive decomposition reactions.

The total SO$_2$ release increases with decreasing particle size of tire rubber and pine wood, as shown in Figure 5-16 and Figure 5-17, respectively. This is also reflected in the magnitude of SO$_2$ concentration peak measured in the analyzers, which is higher for the smallest particles than for the larger particle dimensions. For example, the SO$_2$ concentration peak reaches a maximum of 1413 ppm for the ø 8 mm pine wood particles while 213 and 198 ppm SO$_2$ are measured for wood particles of 13 and 19 mm diameter, under the same conditions, as illustrated in Figure 5-18.
Figure 5-16 shows that tire rubber tends to release more sulfur than pine wood, even though identical energy input is used in the experiments. It is known that the tire rubber follows the conversion pathway I in Figure 3-1 (Larsen, 2007) and experience cracking. It is therefore possible that the tire particle cracks into smaller particles, whereby the tire particle would be in contact with larger surface area of the bed and therefore cause more sulfur release than wood particles, which follows the conversion pathway G in Figure 3-1, in which the char experiences a decrease of particle size.

Thee wood particles were observed to be situated on the top of the bed surface during devolatilization due to the flame front surrounding the fuels particle, which seems to avoid the coverage of the particle under the bed. The particles kept their shape during the devolatilization process and during char oxidation the particle got fragmented due to the mechanical action of the bed. A sketch of the observation is illustrated schematically in Figure 5-19.
The tire rubber particles were also observed to be on top of the bed surface, keeping the particle shape under devolatilization (scenario 1) and char oxidation with some fragmentation (scenario 2, 3 and 4). It was however difficult to visualize the fragmentation due to the angle of visibility from the window. During char combustion, the tire fragmented into several smaller char particles. This is in good agreement with the observations of Nielsen (2012) and Hansens (2011), who observed that tire rubber swells during devolatilization and after gets fragmented.

The carbon conversion for the different dimensions of tire rubber and pine wood are presented in Figure 5-20 and Figure 5-21, respectively. The carbon conversion is much faster for tire rubber than for pine wood and the devolatilization period is not as clear as for pine wood, which may be due to fragmentation. The total conversion time is shorter for the small particles than for the bigger particles for a fixed energy input. This is related to the internal heating up, because the smallest particles are heated faster and releases the volatiles gases faster and with higher concentrations. Consequently, stronger local reducing conditions are formed.

5.3.3 Effect of Degree of Devolatilization of Wood Particles

The pine wood cylinders are pyrolized at different temperatures in order to obtain wood char with different degree of volatiles, as explained in section 5.2.4. All the experiments are performed with the same initial
energy input, 55 kJ, from the virgin wood, which is the non-pyrolyzed wood, in order to enable a direct comparison.

The normalized carbon conversion curves versus time for the different particle sizes are shown from Figure 5-22 to Figure 5-25 for wood char made at 300, 500, 700 and 900 °C, respectively. These curves can be compared to the carbon conversion for the virgin wood at the same conditions, which was presented in Figure 5-21.

For the virgin wood and the wood chars made at different temperatures, the time required for the complete combustion is decreasing in the sequence of one cylinder of 19 mm diameter > 2 cylinders of 13 mm diameter > 5 cylinders of 8 mm diameter. This is the consequence of smaller particles being heated up faster than larger particles due to the internal heat transfer limitations.

For the virgin wood and the wood chars made at different temperatures, the time required for the complete combustion is decreasing in the sequence of one cylinder of 19 mm diameter > 2 cylinders of 13 mm diameter > 5 cylinders of 8 mm diameter. This is the consequence of smaller particles being heated up faster than larger particles due to the internal heat transfer limitations.
The devolatilization period is observed for the virgin wood, and wood chars made at 300 and 500 °C, according to the definition given in the general observations. The average time for complete devolatilization and the char oxidation for virgin wood and the different wood chars of 19, 13, and 8 mm diameters are summarized with the corresponding uncertainties in Figure 5-26 and Figure 5-27, respectively. It should be noted that the virgin wood is considered as being pretreated at 25 °C.
Chapter 5: Sulfur Release during Combustion of Alternative Fuels Particles

The devolatilization period is shortened when the temperature of pre-treatment is increased, which can be explained in terms of the reduced content of volatiles. While the required time to complete char oxidation increases with increasing the temperature of pre-treatment until 500 °C and decreasing from 500 to 900 °C. The same tendency is also seen in the total conversion time for wood char made at 700 and 900 °C, which are shorter than for 500 °C. Monitoring the mass loss of the fuel particle after pyrolysis shows that the char residue decreases for the wood chars made at 700 and 900 °C in comparison with wood char made at 500 °C. The decreased time of char oxidation for these wood chars may be due to their reactivity, which depends on the porosity and the chemical structure (Di Blasi, 2009; Laurendeau, 1978). However, the reactivity has not been further studied because it is considered outside of the scope of this project.

The SO\textsubscript{2} concentration for the 5 cylinders of 8 mm diameter virgin wood and wood char made at 300, 500 and 700 °C experiments is plotted in Figure 5-28. The combustion of wood char made at 700 °C leads to SO\textsubscript{2} concentration of 1-2 ppm, which is insignificant compared to the release of virgin wood and wood char at lower temperatures and the uncertainties related to the thermal decomposition of CuSO\textsubscript{4} and the gas analyzers.

![Figure 5-28: Corrected SO\textsubscript{2} concentration for 5 cylinders of ø 8 mm of virgin wood and char wood made at 300, 500 and 700 °C. Experimental conditions: 900 °C, 5 % fill degree, 2 wt. % CaSO\textsubscript{4}, 100 NL/min, 10 vol. % O\textsubscript{2} in N\textsubscript{2}, 6 rpm. Note: SO\textsubscript{2} concentration from the char at 700 °C cannot be observed.](image)

Hence, SO\textsubscript{2} release is only observed in the cases where devolatilization takes place. During the time of char oxidation there is almost no sulfur release, although the particle releases CO due to the conversion of the char and the combustion is diffusion limited. It may be that the CO from the char oxidation is released in low concentrations, which do not provoke significant sulfur release. Moreover, the oxygen concentration during this period is higher than during devolatilization and the CO may thus be converted faster to CO\textsubscript{2}.

Figure 5-28: Corrected SO\textsubscript{2} concentration for 5 cylinders of ø 8 mm of virgin wood and char wood made at 300, 500 and 700 °C. Experimental conditions: 900 °C, 5 % fill degree, 2 wt. % CaSO\textsubscript{4}, 100 NL/min, 10 vol. % O\textsubscript{2} in N\textsubscript{2}, 6 rpm. Note: SO\textsubscript{2} concentration from the char at 700 °C cannot be observed.

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Figure 5-29 shows the total SO\textsubscript{2} release from the raw materials as a function of the particle size of the combusted virgin wood and wood char made at 300 and 500 °C. The results show that the sulfur release decreases with decreasing degree of conversion. However, it is not possible neither to identify nor quantify which volatile gases that are released in each case because the CO is oxidized in the freeboard atmosphere and the analyzers do not give the possibility to detect other reducing agents.

The total SO\textsubscript{2} release increases, as previously discussed, with decreasing particle size of virgin wood and wood char made at 300 °C. There is a big difference in the SO\textsubscript{2} release for wood char made at 300 and 500 °C due to the degree of fuel conversion at the different temperatures. The total sulfur release for the wood char made at 500 °C is below 1 mg and had almost the same value for the different fuel particle sizes. This is due to the high degree of conversion, whereby few volatile gases are released. It should be remarked that the actual energy input used in the experiments is not constant due to the different content of volatiles.

### 5.3.4 Effect of Sulfur Concentration in the Bed Material

The effect of sulfur concentration in the bed material is investigated using two different concentrations of CaSO\textsubscript{4}, and three different particle diameters of pine wood, all with an energy input of 55 kJ. The experiments are performed at 950 °C using a bed material of 5 % filling degree with 5 wt. % and 2 wt. % CaSO\textsubscript{4}.

Figure 5-30 shows the sulfur release from the raw materials during combustion of pine wood cylinders of 8, 13 and 19 mm diameter in beds containing 5 and 2 wt. % CaSO\textsubscript{4}, and a gas atmosphere with 5 vol. % O\textsubscript{2}. Figure 5-31 shows the sulfur release for the same conditions for a gas atmosphere with 10 vol. % O\textsubscript{2}.

Figure 5-31 shows the sulfur release for the same conditions for a gas atmosphere with 10 vol. % O\textsubscript{2}.

The total SO\textsubscript{2} release increases, as previously discussed, with decreasing particle size of virgin wood and wood char made at 300 °C. There is a big difference in the SO\textsubscript{2} release for wood char made at 300 and 500 °C due to the degree of fuel conversion at the different temperatures. The total sulfur release for the wood char made at 500 °C is below 1 mg and had almost the same value for the different fuel particle sizes. This is due to the high degree of conversion, whereby few volatile gases are released. It should be remarked that the actual energy input used in the experiments is not constant due to the different content of volatiles.
Chapter 5: Sulfur Release during Combustion of Alternative Fuels Particles

5.3.5 Effect of Moisture Content

The effect of moisture content of the wood is studied using wood cylinders of 8 mm diameter with different moisture content. The 30 and 60 wt. % water content is obtained by submerging the wood cylinders in water for different periods. The water content is determined by weighing the wood particles prior and after submersion in water.

Figure 5-32 shows the carbon conversion curves for the dried wood cylinder and wet cylinders with 30 and 60 wt. % of water content. Figure 5-33 shows the sulfur release from the raw materials during the combustion at 900 °C and 10 vol. % O2 of a dry wood cylinder and humidified wood cylinders with 30 and 60 wt. % water content.

The graphs show that the sulfur release increases with increasing sulfur content in the bed. This may be because the volatiles gases are more likely to get in contact with more CaSO4 in the bed and therefore more SO2 is released. The SO2 release decreases with increasing oxygen content for 2 wt. % CaSO4 in the bed because the reducing conditions become less prominent at higher concentrations of O2, but this tendency is less clear for 5 wt. % CaSO4.

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Figure 5-32 shows the carbon conversion curves for the dried wood cylinder and wet cylinders with 30 and 60 wt. % of water content. Figure 5-33 shows the sulfur release from the raw materials during the combustion at 900 °C and 10 vol. % O2 of a dry wood cylinder and humidified wood cylinders with 30 and 60 wt. % water content.
When the moisture content of the wood particles increases, more water must be evaporated and therefore the devolatilization rate decreases. This has also been observed using non-spherical pine wood containing 0, 22 and 40 wt. % moisture in fluidized bed experiments (de Diego et al., 2002). Even though the devolatilization period is prolonged with increasing water content, the full conversion ends at a similar time.

The magnitude of the SO₂ peaks in Figure 5-33 are influenced by the water content. The dry wood cylinder has the highest SO₂ peak, while the SO₂ peaks for the cylinders with a water content of 30 and 60 wt. % have lower values and are wider than the one obtained for the dry wood. The tendency observed is that increasing water content lowers the SO₂ concentration level. This may be due to a delayed devolatilization and the reduced rate of conversion because the volatiles are released at lower concentrations for longer periods, giving rise to lower SO₂ release for a longer time period.

Table 5-7 summarizes the total SO₂ release calculated by equation 5.1 for each case:

<table>
<thead>
<tr>
<th>Table 5-7: Total SO₂ release from the combustion experiments of the single ø 8 mm wood cylinder dried and with 30 and 60 wt. % water content.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dried wood</strong></td>
</tr>
<tr>
<td>Total SO₂ release [mg]</td>
</tr>
</tbody>
</table>

The total SO₂ release differs between the dry wood cylinder and the wet wood cylinders, but the total sulfur release is quite similar for cylinders containing 30 and 60 wt. % water. The release takes more time when the water content is increased from 30 to 60 wt. %, but total amount release is almost the same.
5.3.6 Discussion

The importance of particle size of the fuel has been investigated using pine wood and tire rubber. The results showed that smaller particle sizes gives more SO$_2$ release due to the faster internal heating up while larger particles present more pronounced internal temperature gradients, resulting in a slower heating up. The release and concentration of volatile gases is related to the heating up of the particle. Therefore, higher concentrations of volatiles are released during a shorter period for smaller particles, giving higher concentrations of SO$_2$ release and total SO$_2$ release. Larger particles will release the volatile gases during longer periods, giving lower SO$_2$ concentrations and total SO$_2$ release. Furthermore, the conversion pathway that a fuel type follows and the fragmentation also influence the SO$_2$ release.

The oxygen content in the freeboard atmosphere influences the sulfur release from the bed material. The phase diagram of the sulfur species with oxygen shows that the stability of CaSO$_4$ increases with higher oxygen partial pressure. It may be possible that oxygen influences the reductive decomposition reactions or that the excess oxygen from the freeboard atmosphere oxidizes the reducing agents released from the fuel particle. This influence needs further investigation, which will be conducted in the next chapter.

The effect of particle size on SO$_2$ release is also observed when wood char made at different temperatures are used. SO$_2$ release is only observed for the wood chars containing volatiles and not during char oxidation. This is contradictory to the general experience if coal or petcoke combustion in the calciner is incomplete and is admitted to the industrial kiln inlet causing a dramatically increase of sulfur circulation (Nielsen and Jepsen, 1990). Additional experiments using few grams of granulate wood char (approx. 1 mm diameter) made at 900 °C in the rotary drum provoked a significant SO$_2$ release from the raw materials and the particles following the rolling mode of the material. This shows that the SO$_2$ release is not associated just to devolatilization and is depending on the concentration of the gas released. The CO released during char combustion using wood char made at 700 and 900 °C in the experiments where the degree of devolatilization were investigated, may have not been high enough to provoke SO$_2$ release. Furthermore, the experiments using char wood did not have an actual constant thermal input, only the initial energy input before pyrolysis was constant. Hence, less fuel was introduced when the devolatilization degree was increased. However, in the next chapter this will be further investigated by introduction of the same total amount of gas with different concentrations and time of exposure.

Different phenomena occur simultaneously during the experiments, such as mixing of the fuel with the bed material, heating up of a particle and release of volatiles gases, char combustion, reaction of the reducing agents with CaSO$_4$, and release of SO$_2$. It is not possible to control all of these processes and the current equipment cannot identify and/or quantify the reducing agents released from fuel particles during devolatilization and/or char oxidation. For that reason, the effect of the concentration of different reducing agent in the high temperature rotary drum will be investigated in Chapter 6.

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The effect of the fuel moisture content affects the concentration of the reducing agents by delaying heating up of the particle and by means of dilution by the moisture vapor. The phenomenon may be explained by understanding the effect of the concentration of the reducing agent and this will be further investigated in Chapter 6, however, without addition of H$_2$O (g).

5.4 Conclusions

A literature study of sulfur release during combustion of alternative fuel particles showed that reducing gases from the fuel devolatization cause reductive decomposition of CaSO$_4$ and indicated that fuel particle size is of high importance for the degree of sulfur release.

The sulfur release from raw materials during combustion of tire rubber and pine wood in this chapter was studied using three different particle sizes and the identical energy inputs. The sulfur release from the raw materials increased with decreasing particle size. Tire rubber released more sulfur than pine wood. This may be explained by the conversion pathway of fuel and the mixing of the fuel and raw materials.

The effect of wood cylinders with different degree of volatiles showed that the sulfur release mainly took place during devolatilization, corresponding to the cases with virgin wood and wood chars made at 300 and 500 °C, which contained volatiles. The sulfur release decreased with decreasing degree of conversion.

The sulfur release obtained during the combustion of pine wood increased when the sulfur load in the bed material was increased from 2 to 5 wt. % CaSO$_4$.

In all the experimental series the SO$_2$ release decreases with increasing oxygen concentration due to less prominent reducing conditions at higher O$_2$ concentrations.

The effect of water content was investigated with single wood cylinders with a diameter of 8 mm. The results showed the SO$_2$ peak reaches lower values and the release occurs in a longer time period with increasing water content in a sample, the total amount of sulfur released is however similar for the wet wood cylinder and is less than the dry wood.

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Chapter 5: Sulfur Release during Combustion of Alternative Fuels Particles


FLSmidth A/S; Determination of volatile matter content, Internal report. 2007.


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6. Effect of Different Pyrolysis Gases on Sulfur Release

As mentioned in previous chapters, the main reducing agents (CO, CH₄, and H₂) released from fuel particles under local reducing conditions react with CaSO₄, releasing SO₂. This chapter investigates the effect of the single pyrolyzed gases and their mixtures on sulfur release under the conditions at the inlet of the rotary kiln.

The chapter covers a literature study about the reductive decomposition of CaSO₄ by the main reducing agents released by the fuels. The experimental part describes the modification of the high temperature rotary drum, which allows introduction of reducing agents through a steel tube under the bed material. The experimental results using single reducing agents and binary mixtures are presented in section 6.3.

6.1 Literature Study of the CaSO₄ Reductive Decomposition

The fundamentals of the CaSO₄ reductive decomposition in a wide range of conditions have been studied in relation to chemical-looping combustion, which is a combustion technology for controlling the greenhouse gas emission. Normally, these studies consider CaSO₄ as an oxygen carrier and use two reactors; the first reactor, to reduce CaSO₄ to CaS by a reducing gas, and the second to oxidize CaS by O₂ to CaSO₄. However, side reactions, which reduce CaSO₄ to CaO, exist.

Investigations about sulfur release and capture by limestone at high temperature under fluidized bed (Dam-Johansen and Østergaard, 1991; Hansen et al., 1993) have also suggested the mechanism for sulfur release (reductive decomposition of CaSO₄ on limestone) and capture.

6.1.1 Carbon Monoxide

The reductive decomposition of CaSO₄ by CO has been investigated by many authors (Diaz-Bossio et al., 1985; Kuusik et al., 1985; Oh and Wheelock, 1990; Okumura et al., 2003; Tian and Guo, 2009; Xiao and Song, 2011; Zheng et al., 2011) and can be described by reactions (6-1) and (6-2).

\[
\begin{align*}
\text{CaSO}_4(s) + \text{CO}(g) & \rightarrow \text{CaO}(s) + \text{SO}_2(g) + \text{CO}_2(g) \quad \Delta H_{\text{rxn}}^\circ = -220.0 \text{ kJ/mol} \quad (6-1) \\
\text{CaSO}_4(s) + 4\text{CO}(g) & \rightarrow \text{CaS}(s) + 4\text{CO}_2(g) \quad \Delta H_{\text{rxn}}^\circ = -71.0 \text{ kJ/mol} \quad (6-2)
\end{align*}
\]

Different studies (Kuusik et al., 1985; Oh and Wheelock, 1990; Xiao and Song, 2011) have stated that reaction 6-1 is thermodynamically favored at high reaction temperatures and a low reductive potential of the gas phase, as represented by the ratio of the partial pressures \(P_{\text{CO}}/P_{\text{O}_2}\). When the CO concentration increases, the yield of CaO decreases because the formation of CaS (reaction 6-2) becomes predominant within the temperature of 800-1000 °C (Xiao and Song, 2011). Increasing reaction temperature inhibits the exothermic reaction, reaction (6-2), while greatly promoting the endothermic reaction, reaction (6-1) (Tian and Guo, 2009).
The chemical stability of CaSO₄/CaS/CaO species is dependent on three factors: temperature, SO₂ partial pressure and reductive potential of the gas phase (Shen et al., 2008). The reactivity of the reduction reaction of CaSO₄ by CO has been studied varying these three factors, using isothermal gas (Oh and Wheelock, 1990; Tahakdar et al., 1996; Shen et al., 2008) and non-isothermal methods (Tian et al., 2008; Tian and Guo, 2009), and introducing pure CO or in combination with CO₂, which makes more difficult to compare the results. The majority of the investigations has been carried out in a thermogravimetric analyzer (TGA) or in a fluidized reactor, which is a challenge for the quantitative measurement of the products.

The formation of CaS and CaO with reaction time cannot be clearly distinguished from the overlapped TGA curves due to the simultaneous formation of the two solid compounds. A solution was to connect a FTIR to identify the solid products to the TGA (Shen et al., 2008; Zheng et al., 2011). Using 10 vol. % CO in N₂ at the temperature range between 850-1050 °C, the reaction rate of CaSO₄ reduction was found to increase remarkably with increasing temperature. At 900 °C, no CaO or CaSO₄ were found, only CaS was the reduction product and there was no SO₂ in the flue gas (Shen et al., 2008; Zheng et al., 2011). From 950 °C, no CaSO₄ was found and a small amount of CaO was found. Increasing the reaction temperature, more CaO in the residue product was found. This indicated that the reduction of CaSO₄ with CO predominately occurs via reaction (6-2) in conjunction with reaction (6-1) in the temperature range from 950-1050 °C (Shen et al., 2008) and sulfur emission from the parallel reactions rose (Zheng et al., 2011).

The decomposition of CaSO₄ using a non-isothermal method was studied by Tian and Guo (2009) using five different heating rates (5 to 20 °C/min from 20 to 1200 °C). It was observed that the CaO mole fraction in the products increased with increasing heating rate, which greatly promoted reaction (6-1) and also the side reaction (6-3) (Tian and Guo, 2009).

\[
\text{CaS(s) + 3CaSO}_4(s) \rightarrow 4\text{CaO}(s) + 4\text{SO}_2(g) \quad \Delta H_{\text{rxn}}^{\circ} = 1047.9 \text{ kJ/mol (6-3)}
\]

Consequently, reaction (6-1), which forms CaO and SO₂, proceeds more favorably than reaction (6-2) (Okumura et al., 2003). In agreement, several authors (Wheelock and Boylan, 1960; Kussik et al., 1985; Hayhurst and Tucker, 1992) mentioned that an increase in the reaction temperature and the addition of either CO or O₂ into the system, would promote the decomposition of CaSO₄ to CaO, while an increase of CO would greatly promote reaction (6-1) and also the side reaction (6-3).
concentration promotes the production of CaS. In presence of oxygen, CaS is rapidly oxidized to CaO (Hansen, 1991).

In addition, the presence of O$_2$ showed to inhibit the decomposition of CaSO$_3$ as well as the conversion and the reaction rate, depending on the O$_2$ molar percentage (Tian et al., 2008). The stability of CaSO$_3$ decreases with increasing temperatures and CO content in the gas phase (Tian and Guo, 2009). This is in a good agreement with the phase diagram shown in Figure 5-2. The performance of a cycle test alternating reducing and oxidizing condition at 950 °C in a fluidized bed reactor (Song et al., 2008) discovered the formation of large amounts of SO$_3$ and H$_2$S during the reduction process.

The reaction mechanisms of the reductive decomposition of CaSO$_3$ proposed, based on experimental studies, by Robbins (1966), which has not been available, however it is described by Swift et al. (1976). Oh and Wheelock (1990), and Hansen (1991) with good agreement. First, CO forms an unstable intermediate at the CaSO$_3$ surface, according to reaction (6-4) and desorbs rapidly by the reaction (6-5). The final step in the formation of CaO involves desorption of SO$_2$ (reaction 6-6):

$$\text{CaSO}_3 + \text{CO} \rightarrow \text{CaO} \cdot \text{SO}_2 + \text{CO}_2 \quad (6-4)$$
$$\text{CaO} \cdot \text{SO}_2 + \text{CO} \rightarrow \text{CaO} + \text{SO}_2 \quad (6-5)$$
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A similar mechanism for CaO formation was suggested by Pechkovskii and Ketvo (1961), elaborated by Swift et al. (1976). The reactions from (6-4) to (6-6) are similar to reactions (6-7) and (6-8) with CaO· SO$_2$ written as CaSO$_3$, and based on experimental investigations CaSO$_3$ has been suggested as an important intermediate (Oh and Wheelock, 1990), however its existence is not favored thermodynamically (Hayhurst and Tucker, 1992).

$$\text{CaSO}_3 + \text{CO} \rightarrow \text{CaS} + \text{CO}_2 \quad (6-7)$$
$$\text{CaSO}_3 \rightarrow \text{CaO} + \Delta \text{SO}_2 \quad (6-8)$$

It has been suggested that the formation of CaS from CaSO$_3$ proceeds via CaO as intermediate and nothing indicated that CaS is an intermediate when CaSO$_3$ is converted to CaO (Oh and Wheelock, 1990). Hansen, 1991. However, Oh and Wheelock (1990) do not exclude that some CaSO$_3$ may be converted directly to CaS. The mechanism of CaS formation (suggested by Robbins in 1966) proceeds by reaction (6-9), where adsorbed SO$_3$ on CaO is reduced to elemental sulfur, and the sulfur can then be further reduced to CaS by reaction (6-10) (Swift et al., 1976). Pechkovskii and Ketvo (1961) also proposed a mechanism for CaS formation involving Si, however the reactions were mechanistically unrealistic (Swift et al., 1976).

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The reactivity of methane with calcium sulfate has been studied scarcely (Song et al., 2008; Song et al., 2009). The reactivity of CaSO₄ as oxygen carrier using CH₄ was investigated by Song et al. (2009) where the experiments consisted of six cycles of alternating reducing and oxidizing conditions, in a fixed bed at 950 °C.
for the reducing period and 850 °C for the oxidizing period. The majority of inlet methane reacted with the 
CaSO₄, forming CO₂ and H₂O according to reaction (6-14). Slight amounts of SO₂ were also observed during 
the reducing period and the formation was stated to be mainly due to the solid-solid reaction (6-3). A side 
reaction during the reduction period was also a possibility according to reaction (6-15). The contact between 
CaS and CaSO₄ was enhanced and consequently SO₂ release increased during the initial cycles. H₂S was not 
observed, which indicated that reaction (6-16) did not take place. XRD analysis revealed that CaS was the 
main reduction product, and small amounts of CaO were also formed in the cyclic test.

\[
\text{CaSO}_4(s) + \text{CH}_4(g) \rightarrow \text{CaS}(s) + \text{CO}_2(g) + 2\text{H}_2\text{O}(g) \quad \Delta H_{\text{fus}} = -159.6 \text{ kJ/mol} \tag{6-14}
\]
\[
4\text{CaSO}_4(s) + \text{CH}_4(g) \rightarrow 4\text{CaO}(s) + 4\text{CO}_2(g) + 4\text{SO}_2(g) + 2\text{H}_2\text{O}(g) \quad \Delta H_{\text{fus}} = -1220.8 \text{ kJ/mol} \tag{6-15}
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\text{CaSO}_4(s) + \text{CH}_4(g) \rightarrow \text{CaO}(s) + \text{CO}_2(g) + \text{H}_2\text{S}(g) + 3\text{H}_2\text{O}(g) \tag{6-16}
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The effects of reaction temperature, gas flow rate, sample mass, and particle size on reduction reactions were 
investigated. The conversion of CH₄ increases with high temperature, smaller gas flow rate, larger sample mass 
and smaller particle size (Song et al., 2008).

6.1.4 Alternating Oxidizing and Reducing conditions

In a laboratory scale horizontal tube reactor the release of SO₂ from a synthetic cement calcined raw material 
containing CaSO₄ as sulfur source was quantified as a function of gas atmosphere, alternating oxidizing and 
reducing conditions with CO, H₂ and CH₄ in the temperature range from 900 to 1100 °C (Nielsen, 2012). The 
alternating oxidizing and reducing conditions were applied in intervals of 2 minutes and were repeated over 
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20 minutes. Figure 6-1 shows the results of sulfur release under the alternating oxidizing and reducing 
conditions using different reducing agents.
The results with CO showed an increase in sulfur release with increasing temperature. The sulfur release due to reaction with H$_2$ or CH$_4$ increased from 900 to 1000 °C but decreased at 1100 °C. However, the experiments suffered from mass transfer limitations between the solid material and gas, and the gas analysis system failed to detect H$_2$S, which most probably was formed under the reducing conditions with H$_2$ and CH$_4$. Sulfur mass balances for the experiments were not checked and therefore the effect of the reducing agent on sulfur release was not quantified. A direct comparison between these results and Hansen’s finding, without reductive decomposition (Hansen, 1991), is not possible due to the different conditions of the experiments.

### 6.1.5 Pre-experimental Considerations

From chemical-looping combustion studies of the reductive decomposition of CaSO$_4$, it can be concluded that depending on the temperature and the reducing agent concentration the reduction of CaSO$_4$ can proceed forming CaO or CaS, or a mixture of both products. However, it is difficult to link these studies with the conditions of the rotary kilns because the reducing gases in the kiln will be in contact with the bed material, producing local reducing conditions but the flue gas will not experience the reducing conditions because it is rich in oxygen. For that reason, it is experimentally desired to introduce the reductive gases under a rolling bed material and have an oxidizing atmosphere in the freeboard. In this manner, the H$_2$S or other reduced sulfur species will be oxidized to SO$_2$. In the current facilities and also in the cement plants, there are no analyzers to measure H$_2$S or other reduced sulfur species in the flue gas if these are not oxidized. Furthermore, without an oxidizing atmosphere the reduced sulfur species may react with SO$_2$, which give a wrong measured concentration.
Chapter 6: Effect of Different Pyrolysis Gases on Sulfur Release

Moreover, it was observed during the experiments in Chapter 5 that the fuel particles were on top of the bed during devolatilization. The worst scenario for the sulfur release is when the reducing gases are in contact with the whole bed material. In the high temperature rotary drum it is not possible to force a fuel particle to be converted under the bed. This is another reason for introducing the gases through a steel tube under the bed material.

The reductive decomposition of CaSO₄ with a mixture of two reducing gases have not been investigated previously. So, the main reducing gases released from fuel particles will be first studied individually and then mixtures of them will be used.

6.2 Experimental

The high temperature rotary drum setup has already been presented in section 5.2.1. The setup has been slightly modified for the purpose of the new experiments. The modification consists of removing a thermocouple from the door and through the vacant hole a steel tube in L-shape is inserted in order to introduce reducing agents at the bottom of the material bed. Figure 6-2 shows a schematic 3D view of the modification of the setup. The steel tube is an alloy 600 (75 Ni/16 Cr) which can resist high temperatures. It is bent in an L-shape and the tip is fixed at a distance of 0.5 cm from the bottom of the rotary drum.

Figure 6-2: Schematic 3D view of the modified high temperature rotary drum.

Figure 6-3 illustrates the piping and instrumentation diagram of the modified setup. The tube is connected to a flow line which mixes the nitrogen and two reducing agents. The flowmeters used for the nitrogen and the reducing agents have the capacity of 2 NL/min and 1 NL/min, respectively, and the mixture flow has been set to 1 NL/min, which does not fluidize the bed material. The tube has an internal radius of 1.7 mm, giving a cross-section of 9.08 · 10⁻⁶ m². Thereby, the velocity of the gas introduced under the bed material is 7.22 m/s at 900 °C.

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Chapter 6: Effect of Different Pyrolysis Gases on Sulfur Release

The synthetic mixture of coarse quartz sand and 2 wt. % calcium sulfate is used for a 5 % volumetric filling degree, which corresponds to a bed high of 3 cm. Therefore, the release of the reducing agent takes place 2.5 cm from the top of the bed.

The CO, CH₄ and H₂ are supplied by pressurized 50 L gas bottles with a purity of 99.97 % CO, 99.5 % CH₄ and 50 mol. % H₂ in N₂, respectively. The reducing agents are mixed with nitrogen in order to vary their concentration from 5 vol. % to 40 vol. % and the nitrogen had a purity of 99.999 %.

The procedure followed during these experiments is first to set the flow of N₂ and the flow of the reducing agent sending the mixture to ventilation. When the flow is stable and well mixed, the 3 way valve V16 is turned and the mixture is sent to the high temperature rotary drum and the timer is started for controlling the time of introduction of the reducing agent. When the desired time is reached, the flowmeter of the reducing agent is set to zero and the valve of the reducing agent and the nitrogen are closed. A new experiment is started when the SO₂ and CO₂ concentrations had reached their initial values. Each measurement is repeated 2-3 times to ensure repeatability.

6.3 Results and Discussion

The effect of the single reducing agents on sulfur release is first investigated by varying the concentration introduced, the oxygen content of the freeboard atmosphere and the temperature. It must be emphasized that the SO₂ concentrations plotted in the following graphs do not take into account the thermal decomposition of CaSO₄, i.e. the SO₂ originating from thermal decomposition is set as the baseline. In addition, to resemble a mixture of volatile release from fuels the effect of binary mixtures amongst CO, CH₄ and H₂ on SO₂ release is investigated.

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6.3.1 Carbon Monoxide

6.3.1.1 Effect of the Oxygen Content

The effect of different concentrations of carbon monoxide, from 5 to 20 vol. % CO, on SO\(_2\) release is investigated at 900 °C and at two different oxygen concentrations, 5 and 10 vol. % O\(_2\). The duration of the period where CO is introduced under the bed material for each concentration is 4 or 5 min in order to reach a steady-state and have a constant SO\(_2\) concentration. An example of the constant SO\(_2\) concentration is illustrated in Figure 6-1 in Appendix C. The averages of the constant SO\(_2\) concentrations and the standard deviations of results obtained are presented in Figure 6-4. Lower concentrations than 5 vol. % CO, for example 2 vol. % CO, are tested at 5 vol. % O\(_2\), releasing less than 1 ppm SO\(_2\), which is insignificant compared to the release of 10 ppm SO\(_2\) when 5 vol. % CO is introduced under the bed.

![Figure 6-4](image1)

The SO\(_2\) release at 5 vol. % O\(_2\) is not proportional to the CO concentration introduced. For example, using 10 vol. % CO the release of SO\(_2\) is around 70 ppm, while using 15 vol. % CO the SO\(_2\) concentration is 200 ppm, which is more than the double. Comparing the results at 10 vol. % O\(_2\), SO\(_2\) is released below 100 ppm up to 20 vol. % CO, while at 5 vol. % O\(_2\) the SO\(_2\) release is above 300 ppm SO\(_2\) for 20 vol. % CO. Therefore, it can be seen the sulfur release is reduced when the oxygen content is increased. The corresponding CO\(_2\) concentrations measured for each experiment are plotted in Figure 6-2 in Appendix C.

The carbon mass balance of the experiments performed using CO as reducing agent is checked considering the molar mass flow rate of CO introduced and CO\(_2\) measured by the gas analyzer. The results for the experiments performed at 900 °C with 5 vol. % and 10 vol. % O\(_2\) and at 1000 °C are shown in Appendix C (Table C-1).

![Figure 6-4](image2)
Table C-2, and Table C-3). In the calculations, the CO\textsubscript{2} in the atmospheric air (base line) has been removed from the total CO\textsubscript{2} measured in the outlet. The deviations are within 0.2 and 8 %.

### 6.3.1.2 Effect of the Temperature

The effect of the temperature on sulfur release using CO is also investigated. The previous experiments are performed at 5 vol. % O\textsubscript{2} and at 900 and 1000 °C. Figure 6-5 shows the average SO\textsubscript{2} concentrations with their standard deviation obtained by introducing the different CO concentrations. It can be seen that at 1000 °C the SO\textsubscript{2} release is higher for the same CO concentration, for example, 10 vol. % CO yields an average of 66 ppm SO\textsubscript{2} at 900 °C and 148 ppm SO\textsubscript{2} at 1000 °C. The corresponding CO\textsubscript{2} concentrations measured for each experiment are plotted in Figure C-3 in Appendix C.

Concentrations of 30 vol. % and 40 vol. % CO are also tested at both temperatures. At 900 °C, different SO\textsubscript{2} concentration results were obtained in each repetition, while at 1000 °C the SO\textsubscript{2} release reached concentrations higher than 500 ppm but decreased with time, without reaching a stable concentration and the repeatability of the results were not achieved. The strong reducing conditions may indicate the formation of CaS because after stopping the injection of CO, a SO\textsubscript{2} peak was measured corresponding to CaS oxidation. It was noticed after cooling down the equipment, that the tube outlet was blocked. At these high CO concentrations, CO can react with a steel tube causing carbon deposition, which could be the reason why different SO\textsubscript{2} concentrations were obtained.
6.3.1.3 Effect of the Exposure Time

Since the release of reducing agents from a fuel particle can be very rapid with high concentrations, i.e. during the devolatilization period, or very slow with low concentrations, i.e. during the char oxidation, depending on the volatile and char content, the exposure time of the hot meal to the reducing agents may also vary. Therefore, the time of exposure is investigated by exposing the bed material to the same total amount of CO introduced varying the CO concentration and the injection time.

A total amount of 0.4 L CO is introduced under the bed material using CO concentrations from 5 to 20 vol. % at 900 and 1000 °C. The time required to introduce a total of 0.4 L CO at 5, 7, 10, 15 and 20 vol. % CO is 8 min, 5 min 43 s, 4 min, 2 min 40 s, and 2 min, respectively. Figure 6-6 and Figure 6-7 show the SO$_2$ concentration profiles for the different CO concentrations at 900 and 1000 °C, respectively. As explained in 6.3.1.2, the SO$_2$ release increases with increasing temperature for the same applied CO concentration. The results show that introducing high CO concentrations for a short time gives high concentrations of SO$_2$ but without reaching a stable level such as in the case of 20 vol. % CO. The corresponding CO$_2$: concentration profiles to these experiments are plotted in Figure C-4 and Figure C-5 in Appendix C.

In order to illustrate the influence of the exposure time, the total sulfur release which corresponds to the total integration of the SO$_2$ curves is calculated. Figure 6-8 shows the total SO$_2$ release for the CO concentrations between 5 and 20 vol. % at both temperatures.
Chapter 6: Effect of Different Pyrolysis Gases on Sulfur Release

Figure 6-8: Total SO$_2$ release from the raw material when a total of 0.4 L of CO is introduced under the bed material with different CO concentrations at 900 and 1000 °C. Experimental conditions: flow tube 1 NL/min, 5 % fill degree, 2 wt.% CaSO$_4$, 100 NL/min with 5 vol.% O$_2$, 6 rpm.

Introducing the same total amount of CO, the total SO$_2$ release is different for each CO concentration. For a long exposure of low CO concentrations, the total SO$_2$ release is low compared to the total SO$_2$ release obtained for a short exposure of high CO concentrations. The total SO$_2$ release increases with increasing temperature. At 1000 °C, the main increase in the total SO$_2$ takes place when CO is increased from 5 to 10 vol. %, while at 900 °C, this occurs when CO is increased from 10 to 15 vol. %.

6.3.1.4 Equilibrium Phase Diagrams

The results obtained using CO at 900 °C and 5 vol. % O$_2$ are further used to evaluate the stable phase by using the equilibrium phase diagrams for the SO$_2$-CaO-CaSO$_4$-CaS-CO$_2$ system. Figure 6-9 shows schematically the chemical species of the system. CO is introduced in the bed and forms CO$_2$ and SO$_2$ by reaction with CaSO$_4$, the non-reacted CO is further oxidized to CO$_2$ in the freeboard atmosphere.

Figure 6-9: Sketch of the chemical species in the system.

In the system, it cannot be distinguished whether the CO$_2$ is formed by the reaction with CaSO$_4$, or by oxidation of CO. Since there are two competing reactions, the experimental reducing potentials, $P_{\text{sox}}/P_{\text{CO}}$, for the equilibrium phase diagram are calculated by two different cases: $^{17}$ assuming that CO reacts with CaSO$_4$ only according to reaction (6-1), and $^{18}$ CO reacts only according to reaction (6-2).

Figure 6-9: Sketch of the chemical species in the system.
For the first case, the calculations are done considering only reaction (6-1). The partial pressure of the CO\textsubscript{2} formed by the reaction, $P_{\text{CO}_2\text{react}}$, is equal to the partial pressure of the formed, $P_{\text{SO}_2\text{out}}$, defined by equation 6.1.

The partial pressure of the reacted CO, $P_{\text{CO react}}$, is the difference between the initial CO partial pressure, $P_{\text{CO,in}}$, and the partial pressure of SO\textsubscript{2}, as defined by equation 6.2.

\begin{align*}
CaSO_4(s) + CO(g) &\rightarrow CaO(s) + SO_2(g) + CO_2(g) \\
P_{\text{CO,in}} - P_{\text{SO}_2\text{out}} &\rightarrow P_{\text{CO react}} \text{at equilibrium} \tag{6-2}
\end{align*}

Thereby, the reducing potential at equilibrium is defined by equation 6.3.

\begin{align*}
\frac{P_{\text{CO,in}} - P_{\text{CO}_2\text{react}}}{P_{\text{CO,in}}} &\rightarrow P_{\text{SO}_2\text{in}} \text{at equilibrium} \tag{6.3}
\end{align*}

For each concentration of CO introduced, the CO\textsubscript{2} and SO\textsubscript{2} concentration are measured. The reducing potential at equilibrium is calculated for each experiment and the results are shown in Figure 6-10. For all CO concentrations, the stable phase is CaS.

For the second case, the CO is assumed to react only according to reaction (6-2) and CaS is subsequently oxidized by reaction (6-17).

\begin{align*}
CaSO_4(s) + 4CO(g) &\rightarrow CaS(s) + 4CO_2(g) \tag{6-2}

CaS(s) + \frac{3}{2}O_2(g) &\rightarrow CaO(s) + SO_2(g) \tag{6-17}
\end{align*}
The stoichiometry of reaction (6-2) shows that 4 moles of CO react to give 1 mol of SO\(_2\). Therefore, the partial pressure of CO\(_2\) and CO from the reaction can be calculated according to equation 6.4 and equation 6.5, respectively.

\[
P_{\text{CO}_2,\text{out}} = 4P_{\text{SO}_2,\text{out}} - P_{\text{CO}_2,\text{react}}\quad [6.4]
\]

\[
P_{\text{CO},\text{out}} = 4P_{\text{SO}_2,\text{out}} - 4P_{\text{CO}_2,\text{react}}\quad [6.5]
\]

With the new definitions, the reducing potential at equilibrium can be calculated for each experiment and the results are shown in Figure 6-11. The results are in the stable area of CaS for all CO concentrations. Comparing Figure 6-10 and Figure 6-11, the reducing potential is lower for case 2, where it is assumed that CO reacts by reaction (6-2).

6.3.1.5 Effect of the Rotational Speed

The effect of the rotational speed of the rotary drum, varying from 4 to 20 rpm, has been investigating by injecting 5 vol. % CO at 900 °C and 5 vol. % O\(_2\). Figure 6-12 shows the SO\(_2\) concentration obtained in each case. It seems that the SO\(_2\) release increases with increasing rotational speed, except for the cases of 4 and 6 rpm, however, the difference are few ppm.

![Figure 6-11](image1.png)

![Figure 6-12](image2.png)
The investigation of the influence of CO on SO₂ release has shown that CO concentrations lower than 5 vol. % does not provoke significant SO₂ release, only a few ppm which is insignificant in comparison with the SO₂ concentration from the thermal decomposition of CaSO₄. It seems that there is a minimum concentration below which SO₂ release does not occur and it can be suggested that the SO₂ rate of formation could follow the first order expression, \( r_{SO_2} = k (C_{SO_2}) \), where \( C_{SO_2} \) is the threshold CO concentration below which no SO₂ is released. Kinetic studies of the reductive decomposition of CaSO₄ with CO, summarized in Appendix D, have been performed at different concentrations and temperature ranges by many authors (Diaz-Bossio et al., 1985; Xiao and Song, 2011; Zheng et al., 2011; Kim and Sohn, 2002; Talukdar et al., 1996), however a threshold CO concentration has not been observed.

The effect of the CO concentration can be related to the effect of gases released from alternative fuels. During char combustion, the CO concentration may be quite low, even below 5 vol. % CO, for a long period, and for that reason SO₂ release is not measured. It could be that this minimum CO concentration is dependent on the sulfur content of the bed material. However, this has not been investigated.

The increase of the oxygen concentration resulted in a decrease in SO₂ concentration. This is in agreement with Tian et al. (2008) who stated that the presence of oxygen in the system inhibited the decomposition of CaSO₄ by reducing the reaction rate. In Chapter 5, it was also found that the sulfur release caused by the combustion of pine wood and tire rubber decreased with increasing O₂ content in the gas phase. During devolatization of the solid fuels, the particles were placed on top of the bed and the gases released will be thus oxidized in the proximity of the particle by oxygen because the gas-gas reaction is faster than a gas-solid reaction. Thereby, some of the gases released will not be in contact with the bed material. This means that...
more CO is able to react with CaSO₃ in the experiments when the gas is introduced under the bed material. Hence, the oxygen concentration influences the SO₂ release both when the gases are released under the bed material and in the proximity of the bed material. It is possible that the oxygen diffuses into the bed, oxidizing the reducing agent and consequently influences the SO₂ release. The oxygen concentration next to the bed surface or inside the bed has not been measured; however this would help understanding the conditions that the bed material experiences. In addition, the real cement raw material in the kiln inlet has a lower porosity and higher fill degree than the quartz sand used in these experiments and this can reduce the diffusion of oxygen from the freeboard to the bed.

The percentage of CO introduced that has reacted to SO₂ for each experiment has been calculated by dividing the SO₂ release by the CO injected in molar basis. This ratio has calculated assuming that the reaction is 1:1, following reaction (6-1), due to simplicity and further comparison with the model in Chapter 7. This ratio may however be smaller because the reaction may also take place according to reaction (6-2). Table 6-1 summaries the SO₂/CO percentage for the different CO concentrations, varying the temperature and the O₂ concentration. A minor fraction of CO has reacted to form SO₂, while most of the CO may diffuse to the freeboard atmosphere or may be oxidized to CO₂. The percentage of CO reacted increases with increasing injected CO concentration, temperature and decreasing oxygen concentration.

<table>
<thead>
<tr>
<th>CO conc. [vol. %]</th>
<th>SO₂/CO ratio [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>900°C, 5 vol. % O₂</td>
</tr>
<tr>
<td>5</td>
<td>2.02</td>
</tr>
<tr>
<td>7</td>
<td>2.74</td>
</tr>
<tr>
<td>10</td>
<td>6.67</td>
</tr>
<tr>
<td>15</td>
<td>13.2</td>
</tr>
<tr>
<td>20</td>
<td>16.1</td>
</tr>
</tbody>
</table>

The phase diagram results indicate that CaS is the stable phase for the different CO concentrations used in the present experiment, both when considering reaction (6-1) or reaction (6-2). This is in agreement with the findings of Shen et al. (2008) and Zheng et al. (2011), who found that CaS was the only reduction product at 900°C, while CaO or CaSO₃ were not found. This may indicate that CO preferentially reacts via reaction (6-2) and CaS is fast oxidized to CaO in contact with the oxygen of the freeboard atmosphere releasing SO₂. At higher temperatures, reaction (6-1) may also contribute to the emissions of SO₂. However, in the high temperature rotary drum the composition of the sulfur products in the bed material for each experiment cannot be determined and these products may not be significantly important at the kiln inlet conditions for the cement industry.

Chapter 6: Effect of Different Pyrolysis Gases on Sulfur Release

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Chapter 6: Effect of Different Pyrolysis Gases on Sulfur Release

\[
\begin{align*}
\text{CaSO}_4(s) + CO(g) & \rightarrow CaO(s) + SO_2(g) + CO_2(g) \quad (6-1) \\
\text{CaSO}_4(s) + 4 CO(g) & \rightarrow CaS(s) + 4 CO_2(g) \quad (6-2)
\end{align*}
\]

The results of the investigation regarding the effect of exposure time support the results of the different degrees of devolatilization from Chapter 5. The volatile gases from a fuel particle are released in high concentrations during a short period, while lower CO concentrations for longer time are released during char oxidation or devolatilization of large particles. Keeping the total amount of CO introduced constant, showed that 20 vol. % CO concentration introduced during 2 minutes (representing devolatilization) released a higher total SO\textsubscript{2} release compared to 5 vol. % CO concentration during 8 minutes (representing char combustion or devolatilization of large fuel particles). Thus, the CO concentration and the time of exposure are of high importance for SO\textsubscript{2} release.

An increase of SO\textsubscript{2} release was observed by varying the rotation speed of the rotary drum. The increase of the speed may improve the net contact time of the gas–solid, in other words, the residence time of the gas in the bed increases. Thereby, the CaSO\textsubscript{4} particles may be in more frequent contact with the reducing agent promoting the release of SO\textsubscript{2}.

From the observations of the experiments and the literature review, it is suggested that the conversion of CaSO\textsubscript{4} can give CaS and CaO under reducing conditions and CaS is oxidized to CaO under oxidizing conditions, as illustrated in Figure 6-13. According to Robbins’ reaction mechanism (Swift et al., 1976), the intermediate CaO-SO\textsubscript{2} is responsible for producing either CaO (by reaction (6-6)-i) or CaS (by reaction (6-9) and (6-10)).

Firstly, CaO may be produced but then CaO-SO\textsubscript{2} can react with CO in excess forming directly CaS. The stability of this intermediate may be affected by the temperature, since the CaO, CaS or mixtures of both have been identified in different studies (Shen et al., 2008; Zheng et al., 2011). However, the products were not analyzed in the current study.

![Scheme of the conversion paths of CaSO\textsubscript{4} under reducing and oxidizing conditions.](image)

Figure 6-13: Scheme of the conversion paths of CaSO\textsubscript{4} under reducing and oxidizing conditions.

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Chapter 6: Effect of Different Pyrolysis Gases on Sulfur Release

### 6.3.2 Methane

#### 6.3.2.1 Effect of the Oxygen Content

The effect of different concentrations of methane at different oxygen content is investigated. Figure 6-14 shows the SO$_2$ concentration yielded by the introduction of CH$_4$ concentrations varying from 5 to 40 vol. % at 5 and 10 vol. % O$_2$ of the gas atmosphere and 900 °C.

![Figure 6-14: Effect of different CH$_4$ concentrations introduced under the bed material on SO$_2$ concentration with 5 and 10 vol. % O$_2$. Experimental conditions: flow tube 15 L/min, 900 °C, 3 % H$_2$O, 2 wt. % CaO, 100 NL/min, 6 ppm.](image)

At 5 vol. % O$_2$, the results show that 5 and 10 vol. % CH$_4$ yield SO$_2$ concentrations below 100 ppm. When using 15 and 20 vol. % CH$_4$, the SO$_2$ concentration is between 100 and 200 ppm, and the introduction of 30 and 40 vol. % CH$_4$ yield a SO$_2$ concentrations above 400 ppm, which is the highest SO$_2$ release from the experiments performed with the single reducing agents. When the CH$_4$ concentration is increased from 20 to 30 vol. %, the measured SO$_2$ release increases more than the double.

At 10 vol. % O$_2$, the results show that the SO$_2$ release is lower than 50 ppm when CH$_4$ is introduced under the bed material up to a concentration of 30 vol. %. It can be also seen that when 40 vol. % CH$_4$ is introduced under the bed material, a big increase on the SO$_2$ concentration is observed but the SO$_2$ concentration is in a similar level when 30 vol. % CH$_4$ is introduced at 5 vol. % O$_2$. The corresponding CO$_2$ concentrations measured in the flue gas for each experiment are plotted in Figure C-6 of Appendix C.

#### 6.3.2.2 Effect of the Temperature

The results of SO$_2$ release of the experiments performed at 1000 °C are shown in Figure 6-15. The SO$_2$ release increases with increasing temperature and is more than doubled when the applied CH$_4$ is doubled. The measured CO$_2$ concentration for each experiment is plotted in Figure C-7 of Appendix C.
6.3.2.3 Effect of the Exposure Time

The time of exposure is also investigated using CH₄ as a reducing agent. A total of 0.4 L of CH₄ is introduced under the bed material with CH₄ concentrations varying from 5 to 20 vol. %. These experiments are performed with an oxygen content of 5 vol. % and both at 900 and 1000 °C. Figure 6-16 and Figure 6-17 show the SO₂ concentrations obtained with identical total amount of CH₄ is introduced under the bed material by different CH₄ concentrations at 900 and 1000 °C, respectively. The corresponding CO concentrations for each experiment at 900 and 1000 °C, are shown in Figure C-8 and Figure C-9 in Appendix C, respectively.

![Figure 6-15: Effect of different CH₄ concentrations introduced under the bed material on SO₂ concentration at 900 and 1000 °C. Experimental conditions: flow tube 1 NL/min, 5 % fill degree, 2 wt. % CaSO₄, 100 NL/min with 5 vol. % O₂, 6 rpm.](image)

![Figure 6-16: SO₂ concentrations when a total of 0.4 L CH₄ is introduced under the bed material with 5, 10, 15 and 20 vol. % CH₄ at 900 °C. Experimental conditions: flow tube 1 NL/min, 5 % fill degree, 2 wt. % CaSO₄, 100 NL/min with 5 vol. % O₂, 6 rpm.](image)

![Figure 6-17: SO₂ concentrations when a total of 0.4 L CH₄ is introduced under the bed material with 5, 10, 15 and 20 vol. % CH₄ at 1000 °C. Experimental conditions: flow tube 1 NL/min, 5 % fill degree, 2 wt. % CaSO₄, 100 NL/min with 5 vol. % O₂, 6 rpm.](image)

![Figure 6-18: Effect of the Exposure Time](image)

6.3.2.3 Effect of the Exposure Time

The time of exposure is also investigated using CH₄ as a reducing agent. A total of 0.4 L of CH₄ is introduced under the bed material with CH₄ concentrations varying from 5 to 20 vol. %. These experiments are performed with an oxygen content of 5 vol. % and both at 900 and 1000 °C. Figure 6-16 and Figure 6-17 show the SO₂ concentrations obtained with identical total amount of CH₄ is introduced under the bed material by different CH₄ concentrations at 900 and 1000 °C, respectively. The corresponding CO concentrations for each experiment at 900 and 1000 °C, are shown in Figure C-8 and Figure C-9 in Appendix C, respectively.

![Figure 6-19: Effect of the Exposure Time](image)
CaS was the main product together with small amounts of CaO when using 100 % CH\textsubscript{4}.

Figure 6-18 illustrates the total SO\textsubscript{2} release of the experiments shown in Figure 6-16 and in Figure 6-17 for the different CH\textsubscript{4} concentrations at 900 and 1000 °C. The total SO\textsubscript{2} release increases almost linearly with increasing CH\textsubscript{4} concentration at 1000 °C. On the other hand, at 900 °C the total SO\textsubscript{2} release increases when the CH\textsubscript{4} concentration is increased from 5 to 10 vol. % and for higher concentrations the total SO\textsubscript{2} release remains around the same level.

6.3.2.4 Discussion

In the literature, the decomposition of CaSO\textsubscript{4} has been studied using pure CH\textsubscript{4}. In good agreement with Song et al. (2008), the reaction rate of CH\textsubscript{4} increases with increasing temperature. However, it is not possible to compare the effect of CH\textsubscript{4} concentration and the effect of oxygen content on sulfur release with previous studies. The SO\textsubscript{2} release increases with increasing CH\textsubscript{4} concentration, which is the same trend as with introducing CO. The partial pressure of CH\textsubscript{4} increases when higher concentrations of CH\textsubscript{4} are introduced and this may have a positive effect on the reaction rate of the reactions (6-14) and (6-15).

\[
\begin{align*}
\text{CaSO}_4(s) + \text{CH}_4(g) \rightarrow \text{CaS}(s) + \text{CO}_2(g) + 2\text{H}_2\text{O}(g) & \quad (6-14) \\
4\text{CaSO}_4(s) + \text{CH}_4(g) \rightarrow 4\text{CaO}(s) + \text{CO}_2(g) + 4\text{SO}_2(g) + 2\text{H}_2\text{O}(g) & \quad (6-15)
\end{align*}
\]

CaS was the main product together with small amounts of CaO when using 100 % CH\textsubscript{4} (Song et al., 2008), but it may be that lower CH\textsubscript{4} concentrations will result in a mixture of CaO and CaS, instead of mainly CaS. The same discussion about concentration and oxygen, when CO was introduced, may also be valid for CH\textsubscript{4} since the same tendencies are observed.

Figure 6-18: Total SO\textsubscript{2} release from the raw material when a total of 0.4 L of CH\textsubscript{4} is introduced under the bed material with different CH\textsubscript{4} concentrations at 900 and 1000 °C. Experimental conditions: flow tube 1 NL/min, 5 % fill degree, 2 wt. % CaSO\textsubscript{4}, 100 NL/min with 5 vol. % O\textsubscript{2} in the freeboard gas, 6 rpm.

In good agreement with Song et al. (2008), the reaction rate of CH\textsubscript{4} increases with increasing temperature. However, it is not possible to compare the effect of CH\textsubscript{4} concentration and the effect of oxygen content on sulfur release with previous studies. The SO\textsubscript{2} release increases with increasing CH\textsubscript{4} concentration, which is the same trend as with introducing CO. The partial pressure of CH\textsubscript{4} increases when higher concentrations of CH\textsubscript{4} are introduced and this may have a positive effect on the reaction rate of the reactions (6-14) and (6-15).

\[
\begin{align*}
\text{CaSO}_4(s) + \text{CH}_4(g) \rightarrow \text{CaS}(s) + \text{CO}_2(g) + 2\text{H}_2\text{O}(g) & \quad (6-14) \\
4\text{CaSO}_4(s) + \text{CH}_4(g) \rightarrow 4\text{CaO}(s) + \text{CO}_2(g) + 4\text{SO}_2(g) + 2\text{H}_2\text{O}(g) & \quad (6-15)
\end{align*}
\]

CaS was the main product together with small amounts of CaO when using 100 % CH\textsubscript{4} (Song et al., 2008), but it may be that lower CH\textsubscript{4} concentrations will result in a mixture of CaO and CaS, instead of mainly CaS. The same discussion about concentration and oxygen, when CO was introduced, may also be valid for CH\textsubscript{4} since the same tendencies are observed.
Chapter 6: Effect of Different Pyrolysis Gases on Sulfur Release

Song et al. (2009) conducted their investigations in a fixed bed reactor and stated that SO$_2$ formation is mainly due to solid-solid reaction (6-3) due to a good contact between CaS and CaSO$_4$ (Song et al., 2009). However, a solid-solid reaction is normally quite slow and in a fixed bed reactor there is no mixing enhancing the contact. For that reason, it is not viable that the main SO$_2$ formation is via reaction (6-3). Therefore, the SO$_2$ formation may be mainly due to the formation and oxidation of CaS in contact with the freeboard atmosphere.

$$\text{CaS(s)} + 3\text{CaSO}_4(s) \rightarrow 4\text{CaO(s)} + 4\text{SO}_2(g) \quad (6-3)$$

Formation of H$_2$S was not observed by Song et al. (2009), and in the high rotary drum is not possible to analyze this compound. However, the oxidation of H$_2$S to SO$_2$ would be favored in the rotary drum due to the presence of oxygen and high temperature, but it is still not possible to determine if reaction (6-16) occurred.

$$\text{CaSO}_4(s) + \text{CH}_4(g) \rightarrow \text{CaO(s)} + \text{CO}_2(g) + \text{H}_2\text{S}(g) + 3\text{H}_2\text{O}(g) \quad (6-16)$$

For each experiment of CH$_4$, the percentage of SO$_2$ release relative to the CH$_4$ introduced was calculated in the same way as for CO. The percentage of CH$_4$ reacted may be even smaller if other reactions take place in parallel. Table 6-2 summarizes the SO$_2$/CH$_4$ percentage for the different CH$_4$ concentrations, varying the temperature and the O$_2$ concentration. The results show that a maximum of almost 30% of CH$_4$ reacted to form SO$_2$: Methane in comparison with CO reacts less to form SO$_2$. The percentage of CH$_4$ reacted, which follows the same tendency observed in Table 6-1, increases with increasing injected CH$_4$ concentration, temperature and decreasing oxygen concentration.

Table 6-2: Percentage of SO$_2$ release relative to CH$_4$ injected for different CH$_4$ concentrations varying temperature and O$_2$ content.

<table>
<thead>
<tr>
<th>CH$_4$ conc. [vol. %]</th>
<th>SO$_2$/CH$_4$ ratio [%]: 900 °C 5 vol. % O$_2$</th>
<th>SO$_2$/CH$_4$ ratio [%]: 900 °C 10 vol. % O$_2$</th>
<th>SO$_2$/CH$_4$ ratio [%]: 1000 °C 5 vol. % O$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>2.75</td>
<td>0.43</td>
<td>6.49</td>
</tr>
<tr>
<td>10</td>
<td>6.38</td>
<td>0.62</td>
<td>18.6</td>
</tr>
<tr>
<td>15</td>
<td>6.21</td>
<td>0.54</td>
<td>24.4</td>
</tr>
<tr>
<td>20</td>
<td>7.02</td>
<td>0.71</td>
<td>29.2</td>
</tr>
<tr>
<td>30</td>
<td>13.9</td>
<td>0.76</td>
<td>-</td>
</tr>
<tr>
<td>40</td>
<td>14.8</td>
<td>3.75</td>
<td>-</td>
</tr>
</tbody>
</table>

6.3.3 Hydrogen

The effect of different concentrations of H$_2$ from 5 to 40 vol. %, on SO$_2$ release has been investigated at 900 °C and 5 vol. % O$_2$, as illustrated in Figure 6-19.

Chapter 6: Effect of Different Pyrolysis Gases on Sulfur Release

Song et al. (2009) conducted their investigations in a fixed bed reactor and stated that SO$_2$ formation is mainly due to solid-solid reaction (6-3) due to a good contact between CaS and CaSO$_4$ (Song et al., 2009). However, a solid-solid reaction is normally quite slow and in a fixed bed reactor there is no mixing enhancing the contact. For that reason, it is not viable that the main SO$_2$ formation is via reaction (6-3). Therefore, the SO$_2$ formation may be mainly due to the formation and oxidation of CaS in contact with the freeboard atmosphere.

$$\text{CaS(s)} + 3\text{CaSO}_4(s) \rightarrow 4\text{CaO(s)} + 4\text{SO}_2(g) \quad (6-3)$$

Formation of H$_2$S was not observed by Song et al. (2009), and in the high rotary drum is not possible to analyze this compound. However, the oxidation of H$_2$S to SO$_2$ would be favored in the rotary drum due to the presence of oxygen and high temperature, but it is still not possible to determine if reaction (6-16) occurred.

$$\text{CaSO}_4(s) + \text{CH}_4(g) \rightarrow \text{CaO(s)} + \text{CO}_2(g) + \text{H}_2\text{S}(g) + 3\text{H}_2\text{O}(g) \quad (6-16)$$

For each experiment of CH$_4$, the percentage of SO$_2$ release relative to the CH$_4$ introduced was calculated in the same way as for CO. The percentage of CH$_4$ reacted may be even smaller if other reactions take place in parallel. Table 6-2 summarizes the SO$_2$/CH$_4$ percentage for the different CH$_4$ concentrations, varying the temperature and the O$_2$ concentration. The results show that a maximum of almost 30% of CH$_4$ reacted to form SO$_2$: Methane in comparison with CO reacts less to form SO$_2$. The percentage of CH$_4$ reacted, which follows the same tendency observed in Table 6-1, increases with increasing injected CH$_4$ concentration, temperature and decreasing oxygen concentration.

Table 6-2: Percentage of SO$_2$ release relative to CH$_4$ injected for different CH$_4$ concentrations varying temperature and O$_2$ content.

<table>
<thead>
<tr>
<th>CH$_4$ conc. [vol. %]</th>
<th>SO$_2$/CH$_4$ ratio [%]: 900 °C 5 vol. % O$_2$</th>
<th>SO$_2$/CH$_4$ ratio [%]: 900 °C 10 vol. % O$_2$</th>
<th>SO$_2$/CH$_4$ ratio [%]: 1000 °C 5 vol. % O$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>2.75</td>
<td>0.43</td>
<td>6.49</td>
</tr>
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<td>10</td>
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</tr>
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</tr>
</tbody>
</table>

6.3.3 Hydrogen

The effect of different concentrations of H$_2$ from 5 to 40 vol. %, on SO$_2$ release has been investigated at 900 °C and 5 vol. % O$_2$, as illustrated in Figure 6-19.
The results show that SO₂ concentration increases with increasing H₂ concentration, except from 30 to 40 vol. % H₂ where the SO₂ concentration decreases. The SO₂ concentrations measured are higher than the ones obtained using CO with the same concentration of reducing agent.

### 6.3.3.1 Effect of the Oxygen Content

In a similar experimental series with an oxygen concentration of 10 vol. %, SO₂ release is only observed from 15 vol. % to 30 vol. % H₂, as shown in Figure 6-20. Higher concentrations than of 30 vol. % H₂ are not tested. During the experiments where 5 and 10 vol. % H₂ are introduced under the bed material, no SO₂ is measured and it is observed that the oxygen concentration decreased slightly, meaning that the H₂ is combusted. Comparing Figure 6-19 and Figure 6-20, the SO₂ release has decreased more than half when the oxygen concentration has doubled.

![Figure 6-20: Effect of different H₂ concentrations introduced under the bed material on SO₂ concentration with 10 vol. % O₂. Experimental conditions: flow tube 1 NL/min, 900 °C, 5 % fill degree, 2 wt. % CaSO₄, 100 NL/min, 6 rpm.](image)

The results show that SO₂ concentration increases with increasing H₂ concentration, except from 30 to 40 vol. % H₂ where the SO₂ concentration decreases. The SO₂ concentrations measured are higher than the ones obtained using CO with the same concentration of reducing agent.
6.3.3.2 Effect of the Temperature

Figure 6-21 compares the SO\(_2\) concentration measured for different applied H\(_2\) concentrations at temperatures of 900 and 1000 °C. The sulfur release decreases with increasing temperature, which is not the same trend as observed when introducing CO and CH\(_4\).

**Figure 6-21:** Effect of different H\(_2\) concentrations introduced under the bed material on SO\(_2\) concentration at 900 and 1000 °C. Experimental conditions: flow tube 1 NL/min, 5 vol. % O\(_2\), 5 % fill degree, 2 wt. % CaSO\(_4\), 100 NL/min, 6 rpm.

In Chapter 3, it is mentioned that the hydrogen content released during pyrolysis of biomass increases as the temperature rises (Wu et al., 2009) but on the other hand less SO\(_2\) is released when increasing temperature, even at high H\(_2\) concentrations.

6.3.3.3 Effect of the Exposure Time

The time of exposure is also investigated using H\(_2\) as a reducing agent. At the same conditions as CO and CH\(_4\), a total of 0.4 L of H\(_2\) is introduced under the bed material with a H\(_2\) concentration varying from 5 to 20 vol. %, at 5 vol. % O\(_2\), and at temperatures of 900 and 1000 °C. The results at 900 and 1000 °C are shown in Figure 6-22 and in Figure 6-23, respectively. The results show that the SO\(_2\) release at 1000 °C is lower than for at 900 °C for the same applied H\(_2\) concentration, as also showed in Figure 6-21.

**Figure 6-22:** Effect of different H\(_2\) concentrations introduced under the bed material on SO\(_2\) concentration at 900 °C. Experimental conditions: flow tube 1 NL/min, 5 vol. % O\(_2\), 5 % fill degree, 2 wt. % CaSO\(_4\), 100 NL/min, 6 rpm.

**Figure 6-23:** Effect of different H\(_2\) concentrations introduced under the bed material on SO\(_2\) concentration at 1000 °C. Experimental conditions: flow tube 1 NL/min, 5 vol. % O\(_2\), 5 % fill degree, 2 wt. % CaSO\(_4\), 100 NL/min, 6 rpm.

In Chapter 3, it is mentioned that the hydrogen content released during pyrolysis of biomass increases as the temperature rises (Wu et al., 2009) but on the other hand less SO\(_2\) is released when increasing temperature, even at high H\(_2\) concentrations.

6.3.3.3 Effect of the Exposure Time

The time of exposure is also investigated using H\(_2\) as a reducing agent. At the same conditions as CO and CH\(_4\), a total of 0.4 L of H\(_2\) is introduced under the bed material with a H\(_2\) concentration varying from 5 to 20 vol. %, at 5 vol. % O\(_2\), and at temperatures of 900 and 1000 °C. The results at 900 and 1000 °C are shown in Figure 6-22 and in Figure 6-23, respectively. The results show that the SO\(_2\) release at 1000 °C is lower than for at 900 °C for the same applied H\(_2\) concentration, as also showed in Figure 6-21.
Figure 6-22: SO\(_2\) concentrations when a total of 0.4 L of H\(_2\) is introduced under the bed material with 5, 10, 15 and 20 vol. % H\(_2\) at 900 °C. Experimental conditions: flow tube 1 NL/min, 5 % fill degree, 2 wt. % CaSO\(_4\), 100 NL/min with 5 vol. % O\(_2\), 6 rpm.

Figure 6-23: SO\(_2\) concentrations when a total of 0.4 L of H\(_2\) is introduced under the bed material with 5, 10, 15 and 20 vol. % H\(_2\) at 1000 °C. Experimental conditions: flow tube 1 NL/min, 5 % fill degree, 2 wt. % CaSO\(_4\), 100 NL/min with 5 vol. % O\(_2\), 6 rpm.

Figure 6-24 summarizes the total sulfur release for each H\(_2\) concentration at both temperatures. There is a big increase in the total SO\(_2\) release from 5 to 10 vol. % H\(_2\) at 900 °C and the total SO\(_2\) release is lower for all H\(_2\) concentrations at 1000 °C compared to 900 °C. Short pulses with a high concentration yield higher SO\(_2\) release than long pulses with low concentrations.

Figure 6-24: Total SO\(_2\) release from the raw material when a total of 0.4 L of H\(_2\) is introduced under the bed material with different H\(_2\) concentrations at 900 °C and 1000 °C. Experimental conditions: flow tube 1 NL/min, 5 % fill degree, 2 wt. % CaSO\(_4\), 100 NL/min with 5 vol. % O\(_2\), 6 rpm.

Figure 6-24: Total SO\(_2\) release from the raw material when a total of 0.4 L of H\(_2\) is introduced under the bed material with different H\(_2\) concentrations at 900 °C and 1000 °C. Experimental conditions: flow tube 1 NL/min, 5 % fill degree, 2 wt. % CaSO\(_4\), 100 NL/min with 5 vol. % O\(_2\), 6 rpm.
6.3.3.4 Equilibrium Phase Diagrams

The results obtained using H₂ at 900 °C and 5 vol. % O₂ are used to evaluate the stable phase of the equilibrium phase diagrams for the SO₂-CaO-CaSO₄-CaS-H₂O system. In the same way as for CO, H₂ is introduced in the bed and by reaction with CaSO₄ forms H₂O and SO₂.

Since there are competing reactions and it cannot be distinguished which reactions take place, the experimental reducing potentials, \( P_{\text{red}}/P_{\text{ox}} \), for the equilibrium phase diagram are calculated considering two different approaches: \(^1\) assuming that H₂ reacts with CaSO₄ only according to reaction (6-11), and \(^2\) H₂ reacts only according to reaction (6-12).

\[
\begin{align*}
\text{CaSO}_4(s) + 4 \text{H}_2(g) &\rightarrow \text{CaS}(s) + 4 \text{H}_2\text{O}(g) \quad (6-11) \\
\text{CaSO}_4(s) + \text{H}_2(g) &\rightarrow \text{CaO}(s) + \text{SO}_2(g) + \text{H}_2\text{O}(g) \quad (6-12)
\end{align*}
\]

For the first case, CaS is subsequently oxidized by reaction (6-17).

\[
\text{CaS}(s) + \frac{3}{2} \text{O}_2(g) \rightarrow \text{CaO}(s) + \text{SO}_2(g) \quad (6-17)
\]

The partial pressure of H₂O and H₂ for the reaction (6-11) can be calculated according to equation 6.6 and equation 6.7, respectively. The reducing potential is therefore expressed mathematically by equation 6.8.

\[
\frac{P_{\text{red,ox}}}{P_{\text{ox,red}}} = \frac{4\, P_{\text{SO}_2,\text{out}}}{P_{\text{H}_2,\text{in}}} - 4 \quad [6.6]
\]

\[
\frac{P_{\text{H}_2,\text{in}}}{P_{\text{red,ox}}} = \frac{P_{\text{SO}_2,\text{out}}}{P_{\text{red,ox}}} - 4 \quad [6.7]
\]

\[
\frac{P_{\text{H}_2,\text{in}}}{P_{\text{red,ox}}} = \frac{P_{\text{SO}_2,\text{out}}}{P_{\text{red,ox}}} - 4 \quad [6.8]
\]

For the second scenario, the reducing potential is defined by equation 6.9.

\[
\frac{P_{\text{H}_2,\text{in}}}{P_{\text{red,ox}}} = \frac{P_{\text{SO}_2,\text{out}}}{P_{\text{red,ox}}} - 4 \quad [6.9]
\]

The reducing potentials at equilibrium are calculated for each experiment considering either reaction (6-11) or reaction (6-12), respectively. The corresponding results are shown in Figure 6-25 and Figure 6-26, respectively. The experimental points are in the stable area of CaS for all H₂ concentrations, in the same way as the results with CO. Comparing Figure 6-25 and Figure 6-26, the reducing potentials are slightly lower for case 1, when assuming that H₂ reacts with CaSO₄ forming CaS.
According to the equilibrium phase diagrams, the stable phase under the experimental conditions is CaS, which may interact with SO$_2$.

The formation of H$_2$S via reaction (6-13) may take place, but cannot be detected by the analyzers and the H$_2$S may interact with SO$_2$. However, in an excess of oxygen and at high temperature H$_2$S will oxidize rapidly to SO$_3$ (Montoya et al., 2005).

The experiments investigating the effect of the temperature showed that less SO$_2$ was released at 1000 °C in comparison with the same experiments performed at 900 °C. This is contradictory to the observations of Shen et al. (2008), who stated that the rate of reduction of CaSO$_4$ with H$_2$ increases remarkably with the temperature (Shen et al., 2008). However, this study only investigated the rate of CaSO$_4$ reduction with 5 vol. % H$_2$ and 95 vol. % O$_2$. Considering case 1, the experimental data obtained in the pilot plant setup introducing different H$_2$ concentrations under the bed material is used to show the stable phase in each case.

6.1.3.5 Discussion

The results obtained introducing H$_2$ under the bed showed that the SO$_2$ release increases with increasing H$_2$ concentration. In the literature it is mentioned that reaction (6-11) is favored at reducing potentials (P$_{H_2}$/P$_{H_2O}$) between 10$^{-6}$ and 10$^{-9}$ within the temperature 600-950 °C, while reactions (6-12) and (6-13) are favored at lower reducing potentials (Xiao and Song, 2011; Kim and Sohn, 2002; Shen et al., 2008). On the other hand, according to the equilibrium phase diagrams, the stable phase under the experimental conditions is CaS, which is formed by reaction (6-11) and the subsequent oxidation releases SO$_2$.

\[
\begin{align*}
\text{CaSO}_4(s) + 4H_2(g) &\rightarrow \text{CaS} (s) + 4H_2O (g) \quad (6-11) \\
\text{CaSO}_4(s) + H_2(g) &\rightarrow \text{CaO} (s) + \text{SO}_2(g) + H_2O (g) \quad (6-12) \\
\text{CaSO}_4(s) + 4H_2(g) &\rightarrow \text{CaO} (s) + \text{H}_2S(g) + 3H_2O (g) \quad (6-13)
\end{align*}
\]

The formation of H$_2$S via reaction (6-13) may take place, but cannot be detected by the analyzers and the H$_2$S may interact with SO$_2$. However, in an excess of oxygen and at high temperature H$_2$S will oxidize rapidly to SO$_3$ (Montoya et al., 2005).

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6.1.3.5 Discussion

The results obtained introducing H$_2$ under the bed showed that the SO$_2$ release increases with increasing H$_2$ concentration. In the literature it is mentioned that reaction (6-11) is favored at reducing potentials (P$_{H_2}$/P$_{H_2O}$) between 10$^{-6}$ and 10$^{-9}$ within the temperature 600-950 °C, while reactions (6-12) and (6-13) are favored at lower reducing potentials (Xiao and Song, 2011; Kim and Sohn, 2002; Shen et al., 2008). On the other hand, according to the equilibrium phase diagrams, the stable phase under the experimental conditions is CaS, which is formed by reaction (6-11) and the subsequent oxidation releases SO$_2$.

\[
\begin{align*}
\text{CaSO}_4(s) + 4H_2(g) &\rightarrow \text{CaS} (s) + 4H_2O (g) \quad (6-11) \\
\text{CaSO}_4(s) + H_2(g) &\rightarrow \text{CaO} (s) + \text{SO}_2(g) + H_2O (g) \quad (6-12) \\
\text{CaSO}_4(s) + 4H_2(g) &\rightarrow \text{CaO} (s) + \text{H}_2S(g) + 3H_2O (g) \quad (6-13)
\end{align*}
\]

The formation of H$_2$S via reaction (6-13) may take place, but cannot be detected by the analyzers and the H$_2$S may interact with SO$_2$. However, in an excess of oxygen and at high temperature H$_2$S will oxidize rapidly to SO$_3$ (Montoya et al., 2005).

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vol. % Ni in the temperature range 870–970 °C in a TGA. Therefore, it could be that at temperatures above 970 °C, the rate of CaSO₄ reduction decreases. However, no plausible explanation may be offered based on the present investigations.

The percentage of SO₂ release relative to the H₂ introduced has been calculated as previously described with the other reducing agents. Table 6-3 summaries the SO₂/H₂ percentage for the different H₂ concentrations, varying the temperature and the O₂ concentration. The maximum percentage of H₂ reacted is 15 % at 900 °C and 20 vol. % H₂. In agreement with the graphs, the SO₂ release relative to H₂ injected is below 2 % for the tested H₂ concentrations and decreases when the temperature is increased to 1000 °C.

### Chapter 6: Effect of Different Pyrolysis Gases on Sulfur Release

#### 6.3.4 Carbon Monoxide, Hydrogen, and Methane Comparison

##### 6.3.4.1 Effect of the Concentrations

In the previous section, the effect of the reducing agents on SO₂ release is discussed individually. Comparing the three reducing gases together, the total SO₂ release when a total of 0.4 L of either CO, H₂, or CH₄ using different concentrations is introduced under the bed material at 900 °C and 5 vol. % O₂ is plotted in Figure 6-27. Using the same concentration of reducing agent during the same time, it can be seen that the total SO₂ release is different. The total SO₂ release is around the same level for 5 vol. % CH₄ and 5 vol. % H₂ and a bit lower for 5 vol. % CO. Increasing reducing agent concentration to 10 vol. %, the total SO₂ release yielded by CH₄ and CO is similar and much higher for H₂. At higher reducing agent concentrations, the total SO₂ release is higher when using CO and H₂ and is almost double the total SO₂ for CH₄. So, the introduction of high concentrations of CO and H₂ during a short time leads to high SO₂ release in comparison with the introduction of low concentration of reducing agents for a long time for all these reducing agents.

<table>
<thead>
<tr>
<th>H₂ conc. [vol. %]</th>
<th>900 °C, 5 vol. % O₂</th>
<th>SO₂/H₂ ratio [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>3.03</td>
<td>0.00</td>
</tr>
<tr>
<td>10</td>
<td>12.34</td>
<td>0.00</td>
</tr>
<tr>
<td>15</td>
<td>14.26</td>
<td>0.09</td>
</tr>
<tr>
<td>20</td>
<td>15.46</td>
<td>0.53</td>
</tr>
<tr>
<td>30</td>
<td>12.8</td>
<td>1.54</td>
</tr>
<tr>
<td>40</td>
<td>9.02</td>
<td>-</td>
</tr>
</tbody>
</table>

Chapter 6: Effect of Different Pyrolysis Gases on Sulfur Release
Chapter 6: Effect of Different Pyrolysis Gases on Sulfur Release

6.3.4.2 Effect of Heat of Combustion

The reducing agents used are having different heat of combustion. Reactions (6-18), (6-19) and (6-20) show the combustion reaction and the corresponding heat of combustion. It can be seen that 1 mol of CH₄ gives more than the triple energy than combusting 1 mol of CO or H₂. Therefore, it is desired to investigate how sulfur release is affected by the reducing gases when the same heat of combustion is introduced.

\[
\begin{align*}
\text{CH}_4(g) + 2 \text{O}_2(g) &\rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g) \quad \Delta H = -890 \text{ kJ/mol} \quad (6-18) \\
\text{CO}(g) + \frac{1}{2} \text{O}_2(g) &\rightarrow \text{CO}_2(g) \quad \Delta H = -283 \text{ kJ/mol} \quad (6-19) \\
\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) &\rightarrow \text{H}_2\text{O}(g) \quad \Delta H = -286 \text{ kJ/mol} \quad (6-20)
\end{align*}
\]

Experiments introducing 20 vol. % CO, 18 vol. % CH₄, and 6 vol. % H₂ under the bed material have been performed supplying the energy 0.039 kJ/s and the SO₂ release from these experiments are shown in Figure 6-28. It can be seen proving the same energy, CO gives most sulfur release, 325 ppm, followed by H₂ where the SO₂ release is 120 ppm and the SO₂ release by the injection of CH₄ is around 15 ppm SO₂.
6.3.5 Binary Mixtures

The volatiles gas released during devolatilization of a solid fuel consist of many different gases and the reducing gases are not released only as a single component. The behavior of binary mixtures of CO, CH₄, and H₂ on sulfur release has been investigated.

The binary mixtures with different concentrations of CO, from 0 to 20 vol. %, combined with H₂ and CH₄ in 80 vol. % N₂ have been investigated at the same conditions as in the previous section. The average steady state SO₂ concentration for the different mixture combinations are shown in Figure 6-29. The SO₂ release increases with decreasing CO content in the mixture CO/H₂ but the concentrations are lower than using only 20 vol. % CO or 20 vol. % H₂. For the CO/CH₄ mixture, the highest and the lowest SO₂ concentration are obtained applying 20 vol. % CO in N₂ and 20 vol. % CH₄ in N₂, respectively. The SO₂ concentration increases with increasing CO concentration in the mixture and with decreasing CH₄ concentration. However, the increase is not significant between the intermediate mixtures.

In Appendix C, the average CO₂ concentration profiles for each experiment for both CO/H₂ and CO/CH₄ mixtures are plotted in Figure C-10. The tendency observed is that the CO₂ concentration increases with increasing injected CO concentration.
Chapter 6: Effect of Different Pyrolysis Gases on Sulfur Release

Figure 6-29: SO$_2$ concentrations when mixtures of CO/H$_2$ and CO/CH$_4$ are introduced under the bed material at 900 °C. Experimental conditions: flow tube 1 NL/min, 5 % fill degree, 2 wt. % CaSO$_4$, 100 NL/min with 5 vol. % O$_2$, 6 rpm.

Binary mixtures of different concentrations of CH$_4$ from 0 to 20 vol. %, combined with H$_2$ in 80 vol. % N$_2$, are also investigated. Figure 6-30 shows the average SO$_2$ concentrations released for the mixtures containing CH$_4$. For the CH$_4$/H$_2$ mixture, the highest and the lowest SO$_2$ release concentration are obtained applying 20 vol. % H$_2$ in N$_2$ and 20 vol. % CH$_4$ in N$_2$, respectively. However, the SO$_2$ release is similar for the three mixtures containing 15, 10 and 5 vol. % CH$_4$ and 5, 10 and 15 vol. % H$_2$, respectively. The differences in the SO$_2$ levels between the three intermediate mixtures are so small that no clear tendency can be concluded. Therefore, the SO$_2$ release does not vary significantly with changing the concentration of CH$_4$/H$_2$ mixture.

The measured CO$_2$ concentrations from the binary mixtures containing CH$_4$ are plotted in Figure C-11 in Appendix C.

Figure 6-30: SO$_2$ concentrations when mixtures of CO/H$_2$ and CO/CH$_4$ are introduced under the bed material at 900 °C. Experimental conditions: flow tube 1 NL/min, 5 % fill degree, 2 wt. % CaSO$_4$, 100 NL/min with 5 vol. % O$_2$, 6 rpm.

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Chapter 6: Effect of Different Pyrolysis Gases on Sulfur Release

From the previous results, SO$_2$ concentrations from the binary mixtures containing H$_2$ are plotted in Figure 6-31. The SO$_2$ release increases with increasing H$_2$ concentration when it is mixed with CO, while the SO$_2$ concentration is similar for different mixtures of H$_2$ and CH$_4$.

Figure 6-30: SO$_2$ concentrations when mixtures of CH$_4$/CO and CH$_4$/H$_2$ are introduced under the bed material at 900 °C. Experimental conditions: flow tube 1 NL/min, 5 % fill degree, 2 wt. % CaSO$_4$, 100 NL/min with 5 vol. % O$_2$, 6 rpm.

Figure 6-31: SO$_2$ concentrations when mixtures of H$_2$/CO and H$_2$/CH$_4$ are introduced under the bed material at 900 °C. Experimental conditions: flow tube 1 NL/min, 5 % fill degree, 2 wt. % CaSO$_4$, 100 NL/min with 5 vol. % O$_2$, 6 rpm.
6.3.6 Thermal Decomposition of CaSO₄

During and in between all the experiments, decomposition of CaSO₄ is taking place due to the high operational temperature of the rotary drum. Table 6-4 summarizes the intervals of the SO₂ concentration measured in the analyzers when no reducing gas is introduced at different conditions. The thermal decomposition increases with temperature and decreases with increasing oxygen concentration. The most influencing parameter is the temperature followed by the oxygen content. The rotational speed has a very little influence and the variation is only 1 to 3 ppm, which is insignificant compared to the other parameters.

Table 6-4: SO₂ concentration from thermal decomposition changing temperature, O₂ concentration and rotational speed. Note: *Experiments performed at 5 vol. % O₂ and 6 rpm. **Experiments performed at 900 °C and 6 rpm. ***Experiments performed at 5 vol. % O₂ and 950 °C.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>O₂ conc. [vol. %]</th>
<th>Rotational speed [rpm]</th>
<th>SO₂ conc. [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>50-40</td>
<td>900</td>
<td>5</td>
<td>46</td>
</tr>
<tr>
<td>100-130</td>
<td>1000</td>
<td>10</td>
<td>45</td>
</tr>
<tr>
<td>50-40</td>
<td>20-30</td>
<td>4</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>48</td>
</tr>
</tbody>
</table>

The SO₂ concentration from the thermal decomposition has been subtracted in the previous results shown. However, this concentration contributes significant when the sulfur release by reducing agent is low at higher temperatures.

6.4 Conclusions

Investigations and kinetic studies of reductive decomposition of CaSO₄ by CO, and to less extent H₂ and CH₄ in relation to chemical-looping combustion have reported that CaO, CaS or mixtures of both products are favored, depending on the temperature and the concentration of the reducing gas. The most influencing parameter to the reaction rate of CaSO₄ reduction is the partial pressure of the gaseous reductive agent.

The high temperature rotary drum has been modified in order to introduce reducing gases under the bed material. The effect of different concentrations of CO, H₂, and CH₄ on sulfur release has been experimentally investigated modifying temperature, oxygen content and time of exposure.

Introducing the same total amount with different concentrations has a significant influence. Short pulses with high reducing gas concentrations of reducing as yielded higher concentrations of SO₂ and higher total SO₂ release than long pulses with low reducing gas concentrations.

The experiments using different concentrations of reducing agent, especially CO, indicated that a threshold concentration, below which SO₂ release does not occur, exists.

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<th>Temperature °C</th>
<th>O₂ conc. [vol. %]</th>
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<tbody>
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<td></td>
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<td>10</td>
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Chapter 6: Effect of Different Pyrolysis Gases on Sulfur Release

The SO\textsubscript{2} release increased significantly with increasing temperature, except when H\textsubscript{2} was injected under the bed material. Here the SO\textsubscript{2} release was lower at 1000 °C than at 900 °C.

The percentage of reducing agent that reacted was calculated for each experiment. For CO and CH\textsubscript{4}, the SO\textsubscript{2}/CO increases with increasing injected concentration of CO or CH\textsubscript{4}, temperature and decreasing oxygen concentration. The maximum percentage reached was nearly 30 % when 20 vol. % CH\textsubscript{4} was introduced at 1000 °C and 5 vol. % O\textsubscript{2}. For H\textsubscript{2}, the SO\textsubscript{2} release relative to H\textsubscript{2} injected is below 2 % for the tested H\textsubscript{2} concentrations and decreases when the temperature is increased from 900 to 1000 °C.

Comparing the total SO\textsubscript{2} release using the same concentrations for the three reducing agents, the highest total SO\textsubscript{2} release was obtained using CO at higher concentrations that 10 vol. %, followed by H\textsubscript{2}, while at low concentrations CH\textsubscript{4} and H\textsubscript{2} seem to give higher total SO\textsubscript{2} release than CO. When the same heat of combustion is introduced, the sulfur release is higher using CO and followed by H\textsubscript{2} and CH\textsubscript{4}.

The equilibrium phase diagrams for CO and H\textsubscript{2} were used to evaluate the stable phase using the experimental results and with both reducing agents, CaS was indicated to be the stable phase for the different concentrations.

The experimental results of binary mixtures when CO was present showed that SO\textsubscript{2} increases with increasing CO concentration in the mixture. Similar SO\textsubscript{2} release was obtained for the different mixtures of CH\textsubscript{4} and H\textsubscript{2}.

6.5 References


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6.5 References


Chapter 6: Effect of Different Pyrolysis Gases on Sulfur Release


Chapter 7: Modeling the Sulfur Release in the Inlet of the Rotary Kiln

7. Modeling the Sulfur Release in the Inlet of the Rotary Kiln

The rotary kiln is one of the key components, often referred to as the heart of the cement plant, in the cement industry for converting raw meal to cement clinker. It is the appropriate reactor for manufacturing cement clinker because it has the ability to provide a high temperature environment, appropriate residence time for the clinker reactions and ability to handle solids with a large size distribution. A variety of processes are taking place simultaneously in the rotary kilns, such as particulate mixing, gas-solid and solid phase reactions with intensive heat and mass transfer. The behavior of the rotary kiln is highly nonlinear and very difficult to analyze and control. Measurements are difficult to perform on industrial rotary kilns due to its size and inaccessible design, and theoretical models have been developed for simulating such processes.

This chapter focuses on modeling the sulfur release from the bed material due to combustion of alternative fuels in the inlet of the rotary kiln. First, a review of rotary kilns models for the cement industry is described. In sections 7.2, 7.3, and 7.4, the chosen model approach, the assumptions considered and the model development are explained. The results from the model considering wood as fuel varying different parameters and applying sensitivity analysis are shown and discussed in section 7.5.

7.1 Literature Study on Rotary Kiln Models for the Cement Industry

7.1.1 Review of Rotary Kilns Models

The rotary kiln models based on reaction engineering approach are typically formulated as a counter-current plug flow reactor with two phases: solid and gas (Levenspiel, 1999). Different dynamic models for the behavior of a cement kiln have been developed and can vary from simple descriptive black box models (Sullivan et al., 1927) and one-dimensional models (Spang, 1972; Wittel et al., 2005; Locher, 2009; Sadighi et al., 2011) to more sophisticated physical three-dimensional models based on computational fluid dynamics, CFD (Wang et al., 2006; Ma et al., 2006; Ranade and Mujumdar, 2006; Akhtar et al., 2008; Mujumdar and Ranade, 2008; Svedin et al., 2009).

Several modeling studies of the rotary kiln solid can be found in the literature, including models of particle transport and mixing (Ferron and Singh, 1991; Boateng and Barr, 1996a; Boateng, 2008; Mujumdar and Ranade, 2009), clinker reactions (Spang, 1972; Mastorakos et al., 1999; Mujumdar and Ranade, 2009), and heat transfer phenomena, focusing in radiation heat transfer (Barr et al., 1989; Boateng and Barr, 1996b; Dhanjal et al., 2004; Agustini et al., 2008). In one-dimensional models, the changes in the heat transfer and reaction kinetics for different bed heights are neglected, while the CFD models are limited in their ability to model the clinker chemistry, bed motion, and thermodynamics (Kaantee et al., 2004).
In order to overcome modelling limitations, coupled models, consisting of a one-dimensional model for simulation of the reactions in the bed region and a CFD model for the free board region, have been developed in the last decade (Mastorakos et al., 1999; Lu et al., 2004; Küssel et al., 2009). Advanced simulators programs have also been developed (Mujumdar et al., 2007; Stadler et al., 2011). For example, the Rotary Cement Kiln Simulator software is an integrated reaction engineering based mathematical model for clinker formation and was built by combining separate models for preheater, calciner, rotary kiln and cooler previously developed (Mujumdar et al., 2007).

### 7.1.2 Kiln System Models including Alternative Fuels Usage

The different combustion behavior of alternative fuels has promoted the development of new models for predicting the influence of alternative fuels in kiln system.

The initial rotary kilns models with alternative fuels were developed by the lime industry (Eriksson et al., 1991; Ivarsson and Svedin, 2007; Adams and Svedin, 2008; Svedin et al., 2009) investigating the effect of firing a range of biofuels on the lime kiln performance.

A one-dimensional mathematical model firing full scrap tires dropped into a dry long kiln has been developed (Darabi et al., 2008). The tire combustion model considered that tires were continuously fed into the kiln and absorbed heat through radiation. The different steps of combustion were also taken into account, considering that devolatilization was controlled by external heat transfer and chemical reaction kinetics and char combustion only by oxygen diffusion. This model was incorporated in a CFD cement kiln model, where the calcination process took place in the kiln and reached the calcination temperature in the middle of the kiln. The cement kiln model consisted of different sub-models, such as fluid flow, gas and coal combustion, radiation heat transfer, clinker formation, refractory heat transfer, and NO\(_x\) formation. The kiln simulation predicted the gas temperature, velocity and species concentration inside the kiln, the clinker temperature and composition along the kiln, and the refractory and shell temperatures. The simulation without tire combustion showed a high flame temperature, high NO\(_x\) emissions, and good quality product. Replacing 20 % of the total kiln heat with tires as fuel resulted in a reduced flame temperature, a 33 % reduction of NO\(_x\) emission and good clinker quality. The drop-in location of the tires was a critical factor in mid-kiln tire combustion. The simulation results showed that the drop-in location should be within the calcination zone so that the tire combustion can provide enough energy for the calcination reaction. Further downstream dropping of tires worsened the clinker quality and reduced the kiln efficiency.

The combustion of solid fuels, such as tire rubber and pine wood, fired directly into the material inlet of the industrial rotary kiln was modeled using a reaction engineering approach (Nielsen, 2012). The drying, devolatilization and char oxidations models were combined to estimate conversion times, oxygen consumption, and an approximate gas and bed temperature during fuel conversion. The models may be used...
to estimate how far different fuel particles will be transported into the rotary kiln as a function of particle size and key process parameters. The individual models were validated in a pilot scale rotary drum, however validation of the combined models on an industrial plant was not performed due to the extreme environment and poor accessibility.

Rotary kiln flame models for combustion of alternative fuels through the kiln burner have also developed (Svedin et al., 2009; Haas and Weber, 2010; Nørskov, 2012) using different modeling approaches such as well-stirred reactor model (Haas and Weber, 2010) and as a plug flow reactor (Nørskov, 2012). Hass and Weber focused on the impact of firing RDF on the cement production. The axial dispersion of heat and mass transfer was considered to be controlled by the number of continuous stirred tank reactors (CSTR) in series and the effect of fuel calorific value and the adiabatic flame temperature was modeled as a well-stirred reactor model. Therefore, it is reasonable that the well-stirred reactor model provided very simplified predictions of the energy requirements for varying degrees of RDF substitution. The model did not to take into account recirculation and aerodynamics in the kiln and changes in flame heat transfer when substitution fuels occurred. The model calculations showed that with increasing RDF substitution the position of the flame maximum temperature moved downstream and its value decreased. The influence of changing process parameters were evaluated; i.e. decreasing RDF particle size, increasing the preheated combustion air temperature, using oxygen enrichment, and changing the fuel heating value.

A simplified one-dimensional rotary kiln flame model for combustion of alternative fuels, focusing on describing the flame temperature profile and the fuel combustion time was developed (Nørskov, 2012). The fuel conversion was based on heating, moisture evaporation, devolatilization and char oxidation while it was in suspension. The fuel was heated by convection and radiation from the gas and hot kiln wall but the clinker bed was not included in the model. The model describing co-fired dried sewage sludge and petcoke was validated against experiments performed in a pilot-scale swirl-flow burner setup. Full-scale validation at an industrial cement kiln was not possible due to the inaccessibility of the combustion processes.

The clinker chemistry and thermodynamics in the rotary kiln and the effect of alternative fuels on full scale cement plant was modeled using the commercial software Aspen Plus® (Kaattee et al., 2004). The goal of this model was to be able to select a suitable alternative fuel, optimize process control and alternative fuel consumption, while maintaining the quality of the clinker product. The model divided the full process into segments and determined the effect of alternative fuels on material flows, emissions, and product quality. The calculations for the alternative fuels (meat and bone meal and sewage sludge) were compared to a reference case, where petcoke was used as primary and secondary fuel. Higher amount of air and higher speed of kiln fans were needed during operation with larger amounts of alternative fuels in order to maintain the product quality.
Chapter 7: Modeling the Sulfur Release in the Inlet of the Rotary Kiln

Other models considering solid waste for other usages of rotary kilns, such as rotary kilns incinerators and iron ore reduction process, have been developed (Silcox and Pershing, 1990; Pershing et al., 1993; Ramakrishnan and Sai, 1999; Yang et al., 2004). However, due to the differences of the design and operational system the models cannot be compared with rotary kilns models for the cement industry.

In conclusion, combustion models for alternative fuels in the kiln have been developed in order to evaluate the effect of fuel characteristics, such particle size, process variables, such oxygen content, and clinker quality. However, a model which is able to predict sulfur release when alternative fuels are in contact with the kiln bed material has not been described in the literature.

7.2 System Description and Modeling approach

The aim of the model is to predict sulfur release caused by volatiles from alternative fuels particles fired in the material kiln inlet. The modeling approach of this system consist of modeling the bed material as continuous stirred tank reactors in series where the alternative fuels particles, the volatile gases, and the bed material are well mixed.

In section 7.1, it has been described that well stirred reactors in series are considered for modeling the heat and mass transfer in kiln flame models. This approach has been chosen because it is a simple and engineering approach to evaluate the progress of reactions based on kinetics. Furthermore, when a continuous stirred tank is considered, the rotational speed is taken into account in the model. A computational fluid dynamics approach was not chosen because the system is more complex to define and it has computational limitations with gas-solid reactions together with the turbulent gas flow (Kuipers and van Swaaij, 1998; Paschedag, 2005). If the focus of the model was the physical behavior of the kiln bed, the CFD approach would have been convenient.

The rotary kiln is divided in slices, where each one will be modeled as a CSTR connected in series, as illustrated in Figure 7-1. The initial and final bed temperature and the residence time for the material to go through the rotary kiln are specified in Figure 7-1. The fuel particles are continuously fired in the kiln inlet of the rotary kiln and transported through the different kiln slices.
The model has three steps, which are graphically summarized in Figure 7-2. First, the particle temperature profile is calculated for a single fuel particle. The heating takes place from ambient temperature to 900 °C, which is the temperature of the bed material in the kiln inlet. Secondly, the temperature profile is used to determine the mass loss under pyrolysis corresponding to the volatiles release. Finally, the release of volatiles is used as input in the kiln model, which calculates the consumption of the volatiles, and the formation of the SO$_2$ that will be incorporated in the gas of the freeboard in counter-current.
7.3 Assumptions

The model of heating up and pyrolysis of a fuel particle have been formulated taking into account the following assumptions:

- The fuel particles are spherical.
- The fuel particles are fired directly into the rotary kiln from the surroundings. This means that they are not experiencing preheating.
- The density, heat capacity, and thermal conductivity of the fuel particle are considered constants.
- The fuel particles are converted under pyrolysis (with no oxygen present) in order to calculate the release rate of volatiles.
- The release of volatiles for a single particle is assumed to be additive for the multiple particles.
- The char combustion of the fuel particles is neglected.
- Energy contribution from the fuel particles to the bed material and to the freeboard gas from heating the particles and fuel combustion is neglected.

The kiln model has been formulated taking into account the following assumptions:

- The fuel particles are evenly distributed in the bed material and the release of the volatiles are perfectly mixed with the bed due to the rotation of the rotary kiln. Therefore, the bed material can be modeled as a well-mixed reactor (CSTR), where all the particles in the bed material experience the same conditions.
- Each CSTR is in a steady state, where the temperature and the concentration are homogenous in the whole bed.
- The bed material consists only of CaO particles, which are identical with the same diameter.
- All the sulfur content is assumed to be CaSO₄, which is distributed evenly between all the particles as a shell surrounding the CaO particles.
- The surface area of CaSO₄ does not change with the reaction.
- There is no residence time distribution of the particles of bed material in each CSTR. The bed material is considered that moves from one CSTR to another CSTR.
- A degree of coverage of the fuel is defined to describe the fraction of fuel that is covered by the bed, hence how much of the volatiles is released in the bed and may react with CaSO₄.
- The reaction of CaSO₄ with CO or H₂ follows a 1st order reaction and the kinetic constants have a form of 1st order Arrhenius equation. Since most of the volatile composition is CO, it is assumed that the reaction of CaSO₄ with the volatiles also follows a first order reaction and has a form of 1st order Arrhenius equation. It is assumed that for 1 mol of volatiles consumed, 1 mol of SO₂ is formed, as

Chapter 7: Modeling the Sulfur Release in the Inlet of the Rotary Kiln

- The fuel particles are spherical.
- The fuel particles are fired directly into the rotary kiln from the surroundings. This means that they are not experiencing preheating.
- The density, heat capacity, and thermal conductivity of the fuel particle are considered constants.
- The fuel particles are converted under pyrolysis (with no oxygen present) in order to calculate the release rate of volatiles.
- The release of volatiles for a single particle is assumed to be additive for the multiple particles.
- The char combustion of the fuel particles is neglected.
- Energy contribution from the fuel particles to the bed material and to the freeboard gas from heating the particles and fuel combustion is neglected.

The kiln model has been formulated taking into account the following assumptions:

- The fuel particles are evenly distributed in the bed material and the release of the volatiles are perfectly mixed with the bed due to the rotation of the rotary kiln. Therefore, the bed material can be modeled as a well-mixed reactor (CSTR), where all the particles in the bed material experience the same conditions.
- Each CSTR is in a steady state, where the temperature and the concentration are homogenous in the whole bed.
- The bed material consists only of CaO particles, which are identical with the same diameter.
- All the sulfur content is assumed to be CaSO₄, which is distributed evenly between all the particles as a shell surrounding the CaO particles.
- The surface area of CaSO₄ does not change with the reaction.
- There is no residence time distribution of the particles of bed material in each CSTR. The bed material is considered that moves from one CSTR to another CSTR.
- A degree of coverage of the fuel is defined to describe the fraction of fuel that is covered by the bed, hence how much of the volatiles is released in the bed and may react with CaSO₄.
- The reaction of CaSO₄ with CO or H₂ follows a 1st order reaction and the kinetic constants have a form of 1st order Arrhenius equation. Since most of the volatile composition is CO, it is assumed that the reaction of CaSO₄ with the volatiles also follows a first order reaction and has a form of 1st order Arrhenius equation. It is assumed that for 1 mol of volatiles consumed, 1 mol of SO₂ is formed, as
illustrated in reaction (7-1). The reaction may give a mixture of CaO and CaS as reviewed in Chapter 6, but the oxidation of CaS releasing SO₂ is not considered in the model.

\[ \text{CaSO}_4(s) + \text{Vol}(g) \rightarrow \text{CaO}(s) + \text{CaS}(s) + \text{SO}_2(g) + \text{H}_2\text{O}(g) + \text{CO}_2(g) \]  

(7-1)

- The bed temperature increases linearly from the kiln inlet, 900 °C, to the hot end zone, 1450 °C.
- There is no heat exchange between the bed material and the gas phase and through the kiln shell to the surroundings.
- There is no SO₂ in the gas phase coming from the kiln burner or the evaporation of sulfur in the hot end of the rotary kiln.
- The SO₂ formed in the bed is added to the gas phase.
- The SO₂ in the gas phase does not react either with any other gas species or is absorbed by dust.
- The gas flows of the non-reacted volatiles released and the combustion products to the freeboard gas are neglected.

### 7.4 Mathematical Development

#### 7.4.1 Calculation of the Particle Temperature Profile

The heat up of a large non-isothermal and spherical fuel particle is determined by solving numerically the transient heat transfer differential equation (equation 7.1), because the fuel particles are too large to be considered isothermal.

\[
\frac{\partial T(r,t)}{\partial t} = \frac{1}{\rho_p C_p} \left( \frac{k_p}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T(r,t)}{\partial r} \right) \right) 
\]  

[7.1]

where \( \rho_p \) is the density of the fuel particle in kg/m³, \( C_p \) is the fuel particle heat capacity in J/(kg·K), \( T \) is the temperature in K, \( r \) is the distance from the center in m, and \( k_p \) is thermal conductivity of the fuel particle in W/(m·K).

The initial condition for the fuel particle is expressed by equation 7.2.

\[ T(t=0,r)=T_{ps}=293 \text{K} \]  

[7.2]

The boundary conditions consist of:

- No heat transfer at the center of the particle, which is mathematically expressed by equation 7.3.

\[ \frac{\partial T(r,t)}{\partial r} \bigg|_{r=R_1} = 0 \]  

[7.3]
Chapter 7: Modeling the Sulfur Release in the Inlet of the Rotary Kiln

- The temperature at the fuel particle surface is determined by the heat transfer by conduction with the bed material. Mathematically expressed by equation 7.4.

\[ \dot{k}_p \frac{dT(r-R)}{dr} = h_{cond} (T - T_{b,0}) \]  

where \( T_{b,0} \) is the initial bed temperature in K, which will be the final temperature of the fuel particle, and \( h_{cond} \) is the heat transfer coefficient for conduction in W/(m²K). There parameters are specified in Table 7-1.

### 7.4.2 Calculation of Pyrolysis

The fuel used for this model is wood, so the decomposition of wood material under pyrolysis is described for this material. For other fuels, the decomposition mechanism and the kinetic parameters should probably be changed.

The temperature profiles for the wood particle are used to predict the release of volatiles as a result of the ongoing pyrolysis. Di Blasi (2008) describes the decomposition of wood material to be first order regarding the decomposition of wood and formation of volatiles and char. The general one-component equation for the disappearance of a component during the pyrolysis is presented as dimensionless model by equation 7.5 (Di Blasi, 2008) and it is transformed into a model with dimensions (equation 7.6) to describe the measurable release of volatiles.

\[ \frac{dX}{dt} = -k_{pyr} \cdot (X - X_{\infty}) \]  

Substitution of \( X \) and \( X_{\infty} \), defined as \( X = 1 - \frac{m_{f}}{m_{w,0}} \) and \( X_{\infty} = 1 - \frac{m_{c,0}}{m_{w,0}} \), yields to equation 7.6.

\[ \frac{dm_c}{dt} = -k_{pyr} \cdot (m_c - m_{c,0}) \]  

where \( X \) and \( m_c \) denote the degree of conversion and the remaining mass of wood at time \( t \) in kg, \( X_{\infty} \) and \( m_{c,0} \) are the fraction and the mass which cannot be pyrolyzed, \( m_{f} \) in the initial mass in kg, and \( k_{pyr} \) is kinetic constant for the pyrolysis, which has a form of 1st order Arrhenius equation. The difference between the initial mass and the mass of the particle at any time is the cumulative amount of volatiles released.

### 7.4.3 Rotary Kiln Model

The model development of the rotary kiln model as CSTR in series is based on a steady-state mass balance. The general mass balance for the volatiles is presented in words by equation 7.7.

\[ \text{Accumulation} = \text{In} - \text{Out} + \text{Generation} \]  

\[ \frac{dX}{dt} = -k_{pyr} \cdot (X - X_{\infty}) \]  

Substitution of \( X \) and \( X_{\infty} \), defined as \( X = 1 - \frac{m_{f}}{m_{w,0}} \) and \( X_{\infty} = 1 - \frac{m_{c,0}}{m_{w,0}} \), yields to equation 7.6.

\[ \frac{dm_c}{dt} = -k_{pyr} \cdot (m_c - m_{c,0}) \]  

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### 7.4.3 Rotary Kiln Model

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\[ \text{Accumulation} = \text{In} - \text{Out} + \text{Generation} \]
In = Volatiles from the fuel particle + Volatiles from the previous reactor
Out = Volatiles transferred to next reactor + Volatiles diffusion to freeboard
Generation = − Volatiles consumed by the reaction with CaSO$_4$
Accumulation = Zero due to the steady state assumption

Mathematically, equation 7.7 can be expressed in terms of molar flows, as shown in equation 7.8.

\[
\frac{d \dot{N}}{dt} = (\dot{\bar{n}}_w + \dot{\bar{n}}_{in}) - (\dot{\bar{n}}_{out} + \dot{\bar{n}}_{diff})
\]  \[7.8\]

where $\dot{\bar{n}}_{in}$ is the volatiles molar flow from the previous reactor in mol/s, $\dot{\bar{n}}_{w}$ is the molar flow of the volatiles released from the fuel particle in mol/s, $\dot{\bar{n}}_{out}$ is the volatiles molar flow transferred to the next reactor in mol/s, $\dot{\bar{n}}_{diff}$ is the molar flow of the volatiles that diffuses to the freeboard in mol/s, and $\dot{\bar{n}}_{w}$ is the molar flow of the volatiles released by the reaction with CaSO$_4$ in mol/s. By specifying the mol fluxes, the mol balance for a CSTR $i$ is expressed by equation 7.9.

\[
0 = \dot{Q}_C \bar{C}_{i_{out}} + \dot{Q}_C \bar{C}_{i_{out}}(t) - \dot{Q}_C \bar{C}_{i_{in}} - A_{3D_{avg}} \cdot \dot{k}_3 \cdot \Delta C_3 + k_1 \cdot \Delta C_1 - A_3 \cdot \bar{C}_3
\]  \[7.9\]

where $\bar{C}_i$ is the volatiles concentration flux in the $i$ CSTR in mol/m$^3$, $\bar{C}_{i_{out}}$ is the volatiles concentration flux coming from the previous CSTR in mol/m$^3$, $\bar{C}_{i_{in}}$ is the released volatiles concentration from the fuel in mol/m$^3$, $Q$ is the volumetric flow rate of the volatiles in mol/s, $A_{3D_{avg}}$ is the bed area in contact with the freeboard area in m$^2$, $k_3$ is the volatiles mass transfer coefficient in m/s, $\Delta C_3$ is the difference volatile concentration in the bed ($C_{i_{out}}$) and in the freeboard (which is zero), $k_1$ is the total surface area of sulfur in m$^2$, and $k_{1\leftrightarrow2}$ is the kinetic constant of the reaction between CaSO$_4$ and the volatiles in m/s.

The mass transfer coefficient, $k_3$, is found from a Sherwood correlation. For an industrial rotary kiln, this correlation is used (Coulsdon and Richardson, 1999):

\[
Sh = \frac{k_3 \cdot \bar{C}_{i_{in}}}{D_{3D_{avg}}} = 2 + 0.552 \cdot Re^{0.5} \cdot Sc^{0.5}
\]  \[7.10\]

where $k_{1\leftrightarrow2}$ is the average depth of the bed in m, $D_{3D_{avg}}$ is the effective diffusion coefficient of the volatiles in m$^2$/s, $Re$ is the Reynolds number and $Sc$ is the Schmidt number, which are calculated by the density, the viscosity, and the velocity of the volatile released. The parameters for the volatiles are assumed to be equal to the CO parameters, because CO is the main contribution to the volatile gases. The effective diffusion coefficient of CO in atmospheric, $D_{3D_{avg}}$, is therefore calculated by 7.11.
Chapter 7: Modeling the Sulfur Release in the Inlet of the Rotary Kiln

\[ D_{\text{eff,CO}} = \frac{z}{\varepsilon} D_{\text{CO}} \]  

[7.11]

where \( D_{\text{CO}} \) is diffusion coefficient of CO in atmospheric air in m\(^2\)/s, \( z \) is the bed tortuosity, and \( \varepsilon \) is the bed porosity. Dias et al. (2006) found that the tortuosity, \( \tau \), of a mixed bed of granular particles could be described as \( \tau = 1/\varepsilon \), where \( n \) depends on the particle packing but usually are in the range of 0.4-0.5. The diffusion coefficient of CO in atmospheric air is defined by equation 7.12 (Fueller et al., 1966).

\[ D_{\text{CO}} = \frac{10^{-5} \cdot T^{13} \cdot \left( M_i^i + M_{\text{CO}}^i \right)^{2/3}} { \left( \frac{T_{\text{CO}}}{T_i} \right)^2 \cdot \left( z_{\text{CO}} \right)^{1/2} } \]  

[7.12]

where \( M_i \) is the molar mass of compound \( i \) in g/mol, and \( z \) is the special atomic diffusion volume of compound \( i \) (dimensionless), which are 20.1 for air and 18.9 for CO (Fueller et al., 1966).

The kinetic constant for reaction \( 7-1 \) is defined by equation 7.13. Since most of the volatile composition is CO and the model validation will be with CO, these parameters will are taken from reaction CaSO\(_4\) with CO given by Xiao and Song (2011). These parameters have been chosen because the study of Xiao and Song (2011) was in a temperature range 880-950 °C with high concentrations of CO but without introducing CO\(_2\) (see Appendix D).

\[ k_{\text{CO,vol}} = A_{\text{CO,vol}} \exp \left( \frac{E_{\text{CO,vol}}}{R \cdot T_i} \right) \]  

[7.13]

where \( A_{\text{CO,vol}} \) is the pre-exponential factor in m/s, \( E_{\text{CO,vol}} \) is the activation energy in J/mol, \( R \) is the ideal gas constant in J/(mol·K), and \( T_i \) is the bed temperature in K.

For each CSTR, the bed temperature is calculated according to equation 7.14.

\[ T_{\text{f,b}}(i) = T_{i,b} + \frac{T_{i,b} - T_{\text{f,b}}}{\tau_i} - i \]  

[7.14]

where \( T_{i,b} \) is the final bed temperature in K, \( i \) is the number of CSTRs which are defined for each second, \( N_{\text{CSTR}} \) is the total number of CSTR, and \( \tau_i \) is the bed residence time of the kiln in s.

Since the fuel is converted under pyrolysis, it is assumed that the particle is fully covered by the bed material and therefore the volatiles from the fuel are in contact with the entire bed in the cross-section. In order to include scenarios where the fuel particle is partly covered, the fuel degree of coverage, \( \phi \), is defined from 0 to 1. When the fuel degree of coverage is 1, it means that the entire amount of volatiles released from the fuel
will be in contact with the bed material, while 0 will mean that the volatiles release takes place on top of the bed without reacting with the sulfur. The fuel degree of coverage affects the concentration of volatiles in contact with the bed material according to equation 7.15, giving the apparent volatile concentration from the fuel, \( C_{\text{app}} \):

\[
C_{\text{app}}(t) = C_{\text{vol}}(t) - C_{\text{vol}}(t) (1 - \phi)
\]  

[7.15]

The volatile concentration at steady state for a CSTR \( j \) is found by rearranging equation 7.9 and is given by equation 7.16.

\[
C_{\text{vol}} = \frac{Q(t) \left( C_{\text{in}} + C_{\text{app}}(t) \right)}{\rho_b \cdot v_\text{b} \cdot \left( \phi(t) + \phi_{\text{vol}} \right) \cdot \left( 1 + \chi_\text{v} \right)}
\]  

[7.16]

The number of moles of SO\(_2\) formed is calculated by the difference between the inlet and outlet volatile concentrations in each CSTR, according to equation 7.17. The sulfur consumption is monitored along the kiln and compared to the initial moles of sulfur. The calculations are stopped if all the sulfur content in the bed has been released.

\[
\dot{n}_{\text{SO}_2} = \left[ \phi_{\text{vol}} + \phi_{\text{SO}_2} \right]_{\text{in}} - \left[ \phi_{\text{vol}} + \phi_{\text{SO}_2} \right]_{\text{out}}
\]  

[7.17]

In order to calculate the corresponding SO\(_2\) concentration in the flue gas from the release, the molar flow of flue gas, \( \dot{m}_g \), is calculated according to equation 7.18.

\[
\dot{m}_g = \frac{\rho_{\text{gas}} \cdot \text{massflow}}{M_g}
\]  

[7.18]

where \( \rho_{\text{gas}} \) is the flow of the gas in clinker basis in kg/kg clinker, \( M_g \) is the molar mass of the flue gas in kg/mol, and \( \text{massflow} \) is the solid material flow in kg clinker/s, calculated based on the filling degree and bed velocity as shown by equation 7.19.

\[
\dot{m}_g = \pi \left( \frac{a_k}{2} \right)^2 \cdot F \cdot v_\text{b} \cdot \rho_b
\]  

[7.19]

where \( a_k \) is the diameter of the kiln in m, \( F \) is the fill degree, \( \rho_b \) is the bed density in kg/m\(^3\), and \( v_\text{b} \) is the velocity of the bed in m/s, which is calculated dividing the length of the kiln by the bed residence time required to pass through the entire kiln.
The molar fraction of SO\textsubscript{2} in the flue gas in counter-current, \( y_{SO2,i} \), is calculated according to equation 7.20 and the SO\textsubscript{2} concentration in ppm is then determined by equation 7.21.

\[
y_{SO2,i} = \frac{\theta_{SO2,i}}{\theta_i + \sum \theta_{SO2,j}} \quad \text{for } i = N_{CSTR}, N_{CSTR}-1, \ldots, 1 \tag{7.20}
\]

\[
C_{SO2,i} = \left( \sum y_{SO2,j} \right) 10^6 \quad \text{for } i = N_{CSTR}, N_{CSTR}-1, \ldots, 1 \tag{7.21}
\]

Figure 7-3 schematically illustrates the flows directions and concentrations of volatiles and SO\textsubscript{2}, previously described, for a general three CSTR in series.

The sulfur evaporation factor, \( \varepsilon_s \), is defined by the SO\textsubscript{2} concentrations in the hot meal and in the clinker. For the model sulfur evaporation factor in the kiln inlet, this definition can be estimated in molar basis with the total moles of sulfur released and the initial moles of sulfur that the bed material, as expressed in equation 7.22.

\[
\varepsilon_s = \frac{w_{SO2,hot meal} - w_{SO2,clinker}}{w_{SO2,hot meal}} \times 100 \tag{7.22}
\]

### 7.5 Results

#### 7.5.1 Substitution 10 % Energy with Alternative Fuels fired in the Kiln Inlet

A cement plant with a clinker production of 3500 tons per day is considered. The kiln system is a typical ILC-configuration of a preheater kiln with 5 cyclones and uses 2.993 MJ/kg clinker of which 60 % is fired in the calciner and 40 % in the kiln burner. Ten percent of the energy in the kiln burner, which corresponds to 0.119 MJ/kg clinker, is substituted with fuel fired in the kiln inlet.
The rotary kiln characteristics are 4.35 m of diameter and 51 m of length (FLSMIDTH A/S, 2011) with a fill degree of 10 % and the bed material has a porosity of 0.4. The material residence time is assumed to be 30 minutes, therefore, the corresponding bed velocity along the rotary kiln is 0.025 m/s.

The input parameters for the sub-models: heating up, pyrolysis, and kiln model are specified in Table 7-1. The CO diffusion coefficient and the mass transfer coefficient calculated at 900 °C are listed in order to show their order of magnitude.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood lower heating value [MJ/kg]</td>
<td>LHV</td>
<td>19.7</td>
<td>(Guo et al., 2013)</td>
</tr>
<tr>
<td>Density wood [kg/m³]</td>
<td>ρ</td>
<td>330</td>
<td>(Guo et al., 2013)</td>
</tr>
<tr>
<td>Heat capacity [J/(kg K)]</td>
<td>C_w</td>
<td>1733</td>
<td>(Guo et al., 2013)</td>
</tr>
<tr>
<td>Thermal conductivity [W/(m K)]</td>
<td>k</td>
<td>0.20</td>
<td>(Guo et al., 2013)</td>
</tr>
<tr>
<td>Initial bed temperature [°C]</td>
<td>T_b</td>
<td>900</td>
<td>(Hewlett, 1998)</td>
</tr>
<tr>
<td>Heat transfer coefficient for conduction [W/(m² K)]</td>
<td>h</td>
<td>300</td>
<td>(Linjewile et al., 1993)</td>
</tr>
<tr>
<td>Initial temperature [°C]</td>
<td>T_i</td>
<td>20</td>
<td>Assumed</td>
</tr>
</tbody>
</table>

### Pyrolysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolysis pre-exponential factor [s⁻¹]</td>
<td>A_py</td>
<td>7.68·10⁷</td>
<td>(Reina et al., 1998)</td>
</tr>
<tr>
<td>Pyrolysis activation energy [kJ/mol]</td>
<td>E_a_pyr</td>
<td>124.87·10⁷</td>
<td>(Reina et al., 1998)</td>
</tr>
<tr>
<td>Wood volatiles content [wt. % wood]</td>
<td>w_vol</td>
<td>40</td>
<td>(Nunn et al., 1985)</td>
</tr>
</tbody>
</table>

### Kiln Model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur content [wt. %]</td>
<td>w_s</td>
<td>2</td>
<td>Assumed</td>
</tr>
<tr>
<td>Porosity [-]</td>
<td>α</td>
<td>0.4</td>
<td>Assumed</td>
</tr>
<tr>
<td>Final bed temperature [°C]</td>
<td>T_b</td>
<td>1450</td>
<td>(Hewlett, 1998)</td>
</tr>
<tr>
<td>Pre-exponential factor [m/s]</td>
<td>A_py</td>
<td>14280</td>
<td>(Xiao and Song, 2011)</td>
</tr>
<tr>
<td>Activation energy [kJ/mol]</td>
<td>E_a_py</td>
<td>1890</td>
<td>(Xiao and Song, 2011)</td>
</tr>
<tr>
<td>CO diffusion coefficient at 900 °C [m/s]</td>
<td>D_CO</td>
<td>2.15·10⁻⁵</td>
<td>Calculated</td>
</tr>
<tr>
<td>Mass transfer coefficient at 900 °C [m/s]</td>
<td>k_BC</td>
<td>1.69·10⁻⁸</td>
<td>Calculated</td>
</tr>
</tbody>
</table>

The fuel used to fire in the kiln inlet is wood. The fuel flow required to cover the energy in the kiln inlet is 0.246 kg/s wood. Different particles are defined and their mass and dimension characteristics as well as the number of particles fired are specified in Table 7-2.
Table 7-2: Mass and dimension characteristics of different fuel particles and number of particles fired per second.

<table>
<thead>
<tr>
<th>Particle mass [g]</th>
<th>Particle diameter [mm]</th>
<th>Number of particles /s</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>27.9</td>
<td>8</td>
</tr>
<tr>
<td>15</td>
<td>22.1</td>
<td>16</td>
</tr>
<tr>
<td>10</td>
<td>19.3</td>
<td>25</td>
</tr>
<tr>
<td>5</td>
<td>15.4</td>
<td>49</td>
</tr>
<tr>
<td>1</td>
<td>9.00</td>
<td>246</td>
</tr>
</tbody>
</table>

The temperature profile and the pyrolysis calculation are performed for a single wood particle. The temperature profiles from the center to the surface of a 30 g and 1 g spherical wood particles are plotted in Figure 7-4 and Figure 7-5 at different times. The heating up of the particle of 30 g is quite slow in the center, after 200 seconds the surface temperature is almost 900 °C while the center is just 200 °C. On the contrary, the 1 g wood particle reaches almost 900 °C after 100 seconds.

Figure 7-4: Temperature profiles for a single wood particle of 30 g at 50, 100, 200 and 400 seconds.

Figure 7-5: Temperature profiles for a single wood particle of 1 g at 20, 50 and 100 seconds.

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Figure 7-4: Temperature profiles for a single wood particle of 30 g at 50, 100, 200 and 400 seconds.

Figure 7-5: Temperature profiles for a single wood particle of 1 g at 20, 50 and 100 seconds.

The degrees of devolatilization for the different wood particles, which is calculated based on the mass decrease due to the volatiles release under pyrolysis, are shown in Figure 7-6. The results show that the degree of devolatilization requires longer time to achieve 100 % with increasing particle mass. Moreover, the rate of volatiles release, illustrated in Figure 7-7, is faster and takes place in shorter time with decreasing particle mass.

Chapter 7: Modeling the Sulfur Release in the Inlet of the Rotary Kiln
The SO$_2$ release rate is calculated for each wood particle mass and the results are shown in Figure 7-8. For these calculations, the fuel degree of coverage, $\phi$, is considered to be 1, which means that all the volatiles released from the fuel are in contact with the bed material, and this is the worst case scenario giving the highest SO$_2$ release. The SO$_2$ release rate is higher and lasts shorter time for smaller particles than larger particles. The integration of the SO$_2$ release rate gives the total SO$_2$ release, which is illustrated in Figure 7-9, and determines that more SO$_2$ is released decreasing particle size. This is in good agreement with the experimental results presented in Chapter 5. The particle size affects mainly the release rate but not so much the total release, because the total release is quite similar while the SO$_2$ release rate increases with decreasing particle size.
The SO\textsubscript{2} concentration accumulated in the gas phase in counter-current is calculated as function of the distance from the kiln inlet and the results are plotted in Figure 7-10. Higher SO\textsubscript{2} concentrations in the kiln inlet are obtained with decreasing the mass of the particle. Furthermore, the SO\textsubscript{2} release takes place closer to the kiln inlet with decreasing the wood mass particle. For example, firing 246 wood particles of 1 g the SO\textsubscript{2} release stops before 2 m from the kiln inlet, while firing 8 wood particles of 30 g the sulfur release stops after 12 meters. The different mass particles giving different sizes influence more the distance in the kiln where SO\textsubscript{2} release takes place than the SO\textsubscript{2} concentration in the kiln inlet.

Figure 7-10: SO\textsubscript{2} concentration as function of the distance from the kiln inlet for 8 wood particles of 30 g, 16 wood particles of 15 g, 25 wood particles of 10 g, 49 wood particles of 5 g, and 246 wood particles of 1 g.

Table 7-3 summarizes the time of devolatilization for the different wood particles supplying 10 % of the energy as well as the total SO\textsubscript{2} release, the concentration of SO\textsubscript{2} in the kiln inlet, the sulfur evaporation factor, and the percentage of SO\textsubscript{2} release to CO injected. The time to complete devolatilization increases with increasing particle size, and it is in good agreement with the experimental results of Chapter 5, and the experimental and predicted results of Nielsen (2012). The total SO\textsubscript{2} release and the concentration of SO\textsubscript{2} in the kiln inlet factor increase with decreasing particle mass, and the evaporation factor follows thereby the same tendency. The SO\textsubscript{2} release relative to the CO injected is nearly 100 % indicating that almost all CO reacts with CaSO\textsubscript{4} for the different scenarios.
Chapter 7: Modeling the Sulfur Release in the Inlet of the Rotary Kiln

Table 7-3: Summary of the time of devolatilization, total SO$_2$ release, SO$_2$ concentration in the kiln inlet, sulfur evaporation factor, and the percentage of SO$_2$ release to CO injected for the different mass particles with the same energy input.

<table>
<thead>
<tr>
<th>Particle mass [g]</th>
<th>Particle diameter [mm]</th>
<th>Time of devolatilization [s]</th>
<th>Total SO$_2$ release [g]</th>
<th>Conc. SO$_2$ in kiln inlet [ppm]</th>
<th>$\varepsilon$ [%]</th>
<th>SO$_2$/CO ratio [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>27.9</td>
<td>340</td>
<td>76.46</td>
<td>1072</td>
<td>3.27</td>
<td>99.9</td>
</tr>
<tr>
<td>15</td>
<td>22.1</td>
<td>230</td>
<td>77.34</td>
<td>1087</td>
<td>3.77</td>
<td>99.9</td>
</tr>
<tr>
<td>10</td>
<td>19.3</td>
<td>180</td>
<td>80.13</td>
<td>1134</td>
<td>3.93</td>
<td>99.9</td>
</tr>
<tr>
<td>5</td>
<td>15.4</td>
<td>120</td>
<td>81.02</td>
<td>1141</td>
<td>3.96</td>
<td>99.9</td>
</tr>
<tr>
<td>1</td>
<td>9.00</td>
<td>44.0</td>
<td>81.88</td>
<td>1181</td>
<td>4.10</td>
<td>99.9</td>
</tr>
</tbody>
</table>

7.5.1.1 Effect of the Fuel Degree of Coverage

The effect of the fuel degree of coverage is investigated using 25 wood particles of 10 g corresponding to 10 % energy input. This particle size is chosen because it is an intermediate size and it is reasonable to be used in the industry. Figure 7-11 and Figure 7-12 show the effect of the fuel degree of coverage on the SO$_2$ release rate and the SO$_2$ concentration as function of the distance from the kiln inlet, respectively. The SO$_2$ release rate and the SO$_2$ concentration decrease with decreasing fuel degree of coverage because less volatiles are in contact with the bed material and consequently less volatiles can react with CaSO$_4$ releasing SO$_2$.

The total SO$_2$ release, the SO$_2$ concentration in the kiln inlet, the sulfur evaporation factor, and the percentage of SO$_2$ release to CO injected for the different degree of coverage are specified in Table 7-4.

7.5.1.1 Effect of the Fuel Degree of Coverage

The effect of the fuel degree of coverage is investigated using 25 wood particles of 10 g corresponding to 10 % energy input. This particle size is chosen because it is an intermediate size and it is reasonable to be used in the industry. Figure 7-11 and Figure 7-12 show the effect of the fuel degree of coverage on the SO$_2$ release rate and the SO$_2$ concentration as function of the distance from the kiln inlet, respectively. The SO$_2$ release rate and the SO$_2$ concentration decrease with decreasing fuel degree of coverage because less volatiles are in contact with the bed material and consequently less volatiles can react with CaSO$_4$ releasing SO$_2$. 

The total SO$_2$ release, the SO$_2$ concentration in the kiln inlet, the sulfur evaporation factor, and the percentage of SO$_2$ release to CO injected for the different degree of coverage are specified in Table 7-4.
The three variables are highest when the fuel particle is fully covered by bed material ($\phi=1$), because the contact between the CO concentration and the CaSO$_4$ in the bed material is higher. The sulfur evaporation factor decreases linearly with decreasing the fuel degree of coverage.

The fuel degree of coverage is a parameter, which cannot be directly controlled, because it depends on the mixing between fuel particles with the bed material. Nielsen (2012) investigated experimentally the mixing of large and small particles in rotary kilns and showed that the degree of visibility above the bed depends on the material fill degree, the dimensions and sphericity of the fuel particle, and the fuel density. A probability correlation was derived dependent on the characteristics of the bed, the sphericity and the density of the fuel, and fitting parameters from the conducted experiments at room temperature (Nielsen, 2012). The tendency at room temperature was that large fuel particles were more visible than smaller fuel particles, however, this correlation has not been validated at temperatures relevant for the cement rotary kilns.

### 7.5.1.2 Effect of the Fill Degree

The fill degree of the kiln bed has been modified in order to investigate its influence on SO$_2$ release when firing 25 wood particle of 10 g. Figure 7-13 shows the SO$_2$ release rate, the total SO$_2$ release, and the concentration of SO$_2$ when the bed material has a fill degree of 20, 10, and 5 % with the same sulfur concentration, 2 wt. %, in each case. Graph a) shows that the SO$_2$ release rate is the same for the different fill degrees because nearly 100 % of volatiles gases reacted with the sulfur in the bed, which is in excess. The total SO$_2$ release, illustrated in graph b), is equal for the different fill degrees. The SO$_2$ concentration as function of the distance from the kiln inlet, graph c), increases with decreasing fill degree, this is because the material bed flow is decreased and consequently the gas flow also decreases, according to equations 7.16 and 7.17.
Chapter 7: Modeling the Sulfur Release in the Inlet of the Rotary Kiln

The summary of the SO₂ release, the SO₂ concentration in the kiln inlet, the sulfur evaporation factor, and the percentage of SO₂ release to CO injected for the scenarios varying the bed fill degree containing the same sulfur concentration is shown in Table 7-5. The total SO₂ release is the same for the different bed fill degrees as illustrated in Figure 7-13, because the CaSO₄ is reactant in excess for the three cases. This means that the same volatile concentration gives the same SO₂ release, but the concentration in the gas phase is different, because the gas flow depends on the solid material flow, which is a function of the fill degree. The highest SO₂ concentration in the kiln inlet and the sulfur evaporation factor correspond to 5 % fill degree, while the lowest SO₂ concentration in the kiln inlet and sulfur evaporation factor to 20 % fill degree.

Table 7-5: Summary of the SO₂ release, SO₂ concentration in the kiln inlet, sulfur evaporation factor, and the percentage of SO₂ release to CO injected for the scenarios varying the bed fill degree using 25 wood particles of 10 g.

<table>
<thead>
<tr>
<th>Fill degree [%]</th>
<th>Total SO₂ release [g]</th>
<th>Conc. SO₂ in kiln inlet [ppm]</th>
<th>ε [%]</th>
<th>SO₂/CO ratio [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>80.13</td>
<td>2281</td>
<td>7.92</td>
<td>99.9</td>
</tr>
<tr>
<td>10</td>
<td>80.13</td>
<td>1134</td>
<td>3.93</td>
<td>99.9</td>
</tr>
<tr>
<td>20</td>
<td>80.13</td>
<td>570.9</td>
<td>1.98</td>
<td>99.9</td>
</tr>
</tbody>
</table>

The summary of the SO₂ release, the SO₂ concentration in the kiln inlet, the sulfur evaporation factor, and the percentage of SO₂ release to CO injected for the scenarios varying the bed fill degree containing the same sulfur concentration is shown in Table 7-5. The total SO₂ release is the same for the different bed fill degrees as illustrated in Figure 7-13, because the CaSO₄ is reactant in excess for the three cases. This means that the same volatile concentration gives the same SO₂ release, but the concentration in the gas phase is different, because the gas flow depends on the solid material flow, which is a function of the fill degree. The highest SO₂ concentration in the kiln inlet and the sulfur evaporation factor correspond to 5 % fill degree, while the lowest SO₂ concentration in the kiln inlet and sulfur evaporation factor to 20 % fill degree.

Table 7-5: Summary of the SO₂ release, SO₂ concentration in the kiln inlet, sulfur evaporation factor, and the percentage of SO₂ release to CO injected for the scenarios varying the bed fill degree using 25 wood particles of 10 g.

<table>
<thead>
<tr>
<th>Fill degree [%]</th>
<th>Total SO₂ release [g]</th>
<th>Conc. SO₂ in kiln inlet [ppm]</th>
<th>ε [%]</th>
<th>SO₂/CO ratio [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>80.13</td>
<td>2281</td>
<td>7.92</td>
<td>99.9</td>
</tr>
<tr>
<td>10</td>
<td>80.13</td>
<td>1134</td>
<td>3.93</td>
<td>99.9</td>
</tr>
<tr>
<td>20</td>
<td>80.13</td>
<td>570.9</td>
<td>1.98</td>
<td>99.9</td>
</tr>
</tbody>
</table>
7.5.1.3 Effect of CaSO\textsubscript{4} Content in the Bed Material

The effect of sulfur content in the bed material on sulfur release is studied using 25 wood particles of 10 g. Figure 7-14 shows the results of the SO\textsubscript{2} release rate, the total SO\textsubscript{2} release, and the SO\textsubscript{2} concentration in the gas phase, which are not modified by the variation of sulfur content. This can be explained by the reaction of nearly 100% of the volatiles with CaSO\textsubscript{4} in excess. Furthermore, the variation of the surface area of sulfur for each case is insignificant and not influences the output results. However, this is not in good agreement with the experimental finding from Chapter 5 (Figure 5-30 and Figure 5-31).

The sulfur evaporation factor is calculated in each case and significantly increases with decreasing sulfur content, as illustrated in Table 7-6. That is because the fraction gets larger if the initial sulfur amount is lower and the same amount of sulfur is released.

Table 7-6: Summary of the total SO\textsubscript{2} release, SO\textsubscript{2} concentration in the kiln inlet, sulfur evaporation factor, and the percentage of SO\textsubscript{2} release to CO injected for different sulfur bed content using 25 wood particles of 10 g.

<table>
<thead>
<tr>
<th>CaSO\textsubscript{4} in bed material [wt. %]</th>
<th>Total SO\textsubscript{2} release [g]</th>
<th>Conc. SO\textsubscript{2} in kiln inlet [ppm]</th>
<th>ε\textsubscript{s} [%]</th>
<th>SO\textsubscript{2}/CO ratio [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>80.13</td>
<td>1134</td>
<td>36.68</td>
<td>99.9</td>
</tr>
<tr>
<td>2</td>
<td>80.13</td>
<td>1134</td>
<td>3.93</td>
<td>99.9</td>
</tr>
<tr>
<td>5</td>
<td>80.13</td>
<td>1134</td>
<td>1.78</td>
<td>99.9</td>
</tr>
</tbody>
</table>
7.5.2 Effect of Firing Degree in the Kiln Inlet

The firing degree is the rate of energy substituted in the kiln inlet. The effect of the firing degree in the kiln inlet on sulfur release is also investigated when wood particles of 10 g are fired under the bed material with 10 % fill degree and 2 wt. % CaSO₄. The modification of the firing degree varies the number of wood particles used in order to satisfy the fuel flow required to cover the energy in the kiln inlet. Figure 7-15 shows the SO₂ release rate, the total SO₂ release, and the SO₂ concentration in the kiln inlet for the scenarios of 5 and 15 % firing degree in the kiln inlet and compared to the 10 %. The numbers of wood particles of 10 g required are 12, 25, and 37 for 5, 10, and 15 % firing degree, respectively. The SO₂ release rate, the total SO₂ release, and the SO₂ concentration increase with increasing substitution energy. This observation is in good agreement with the experimental results of Nielsen (2012) investigating the energy input on sulfur release, which were presented in Figure 5-7.

The corresponding total SO₂ release, SO₂ concentrations in the kiln inlet, sulfur evaporation factors and the percentages of SO₂ release to CO injected in the kiln inlet for the different firing degree scenarios are listed in Table 7-7. The total SO₂ release and the SO₂ concentration in the kiln inlet increase with increasing energy.
substitution, because the volatiles gases in contact with the sulfur bed material also increases. Consequently, the sulfur evaporation factor increases.

Table 7-7: Summary of the total SO\textsubscript{2} release, SO\textsubscript{2} concentration in the kiln inlet, sulfur evaporation factor, and the percentage of SO\textsubscript{2} release to CO injected for different firing degree scenarios using wood particles of 10 g.

<table>
<thead>
<tr>
<th>Firing degree in kiln inlet [%]</th>
<th>Total SO\textsubscript{2} release[g]</th>
<th>Conc. SO\textsubscript{2} in kiln inlet [ppm]</th>
<th>ε\textsubscript{s} [%]</th>
<th>SO\textsubscript{2}/CO ratio [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>38.89</td>
<td>548.1</td>
<td>1.90</td>
<td>99.9</td>
</tr>
<tr>
<td>10</td>
<td>80.13</td>
<td>1134</td>
<td>3.93</td>
<td>99.9</td>
</tr>
<tr>
<td>15</td>
<td>119.9</td>
<td>1668</td>
<td>5.86</td>
<td>99.9</td>
</tr>
</tbody>
</table>

7.5.3 Sensitivity analysis

A sensitivity analysis is performed to evaluate the importance of the input variables in the kiln model on the carbon monoxide concentration in the kiln inlet. This method only addresses sensitivity relative to the chosen reference case, but parameter interactions are not evaluated. The input parameters for a chosen reference case are specified in Table 7-8 as well as the output results.

Table 7-8: Input parameters and output results for the reference case.

<table>
<thead>
<tr>
<th>Input parameter</th>
<th>Symbol</th>
<th>Reference value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass particle [g]</td>
<td>(m_b)</td>
<td>10</td>
</tr>
<tr>
<td>Sulfur input [wt.]</td>
<td>(w_{\text{in}})</td>
<td>2</td>
</tr>
<tr>
<td>Fill degree [%]</td>
<td>F</td>
<td>10</td>
</tr>
<tr>
<td>Bed porosity [-]</td>
<td>(\phi)</td>
<td>0.4</td>
</tr>
<tr>
<td>Degree of coverage [-]</td>
<td>(\phi)</td>
<td>0.7</td>
</tr>
<tr>
<td>Activation energy [kJ/mol]</td>
<td>(E_{\text{a,Vol}})</td>
<td>14280</td>
</tr>
<tr>
<td>Pre-exponential factor [m/s]</td>
<td>(A_{\text{Vol}})</td>
<td>1890</td>
</tr>
<tr>
<td>Firing degree [%]</td>
<td>-</td>
<td>10</td>
</tr>
</tbody>
</table>

Each input parameter is changed with +/- 25 % while keeping the remaining parameters constant. Table 7-9 summarizes the output results obtained for each case, and their percentage deviation from the output results obtained to the reference case. The results show that the parameters with the largest influence on the three output variables are the firing degree and the fuel degree of coverage. On the contrary, the activation energy and the pre-exponential factor do not influence the output results. The variation of +/- 25 % of the sulfur bed content influences only the evaporation factor, because the variation of the initial bed properties affects the sulfur evaporation factor increases. Consequently, the sulfur evaporation factor increases.

Table 7-9: Summary of the total SO\textsubscript{2} release, CO concentration in the kiln inlet, sulfur evaporation factor, and the percentage of SO\textsubscript{2} release to CO injected for different firing degree scenarios using wood particles of 10 g.

<table>
<thead>
<tr>
<th>Firing degree in kiln inlet [%]</th>
<th>Total SO\textsubscript{2} release[g]</th>
<th>Conc. SO\textsubscript{2} in kiln inlet [ppm]</th>
<th>ε\textsubscript{s} [%]</th>
<th>SO\textsubscript{2}/CO ratio [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>38.89</td>
<td>548.1</td>
<td>1.90</td>
<td>99.9</td>
</tr>
<tr>
<td>10</td>
<td>80.13</td>
<td>1134</td>
<td>3.93</td>
<td>99.9</td>
</tr>
<tr>
<td>15</td>
<td>119.9</td>
<td>1668</td>
<td>5.86</td>
<td>99.9</td>
</tr>
</tbody>
</table>

Each input parameter is changed with +/- 25 % while keeping the remaining parameters constant. Table 7-9 summarizes the output results obtained for each case, and their percentage deviation from the output results obtained to the reference case. The results show that the parameters with the largest influence on the three output variables are the firing degree and the fuel degree of coverage. On the contrary, the activation energy and the pre-exponential factor do not influence the output results. The variation of +/- 25 % of the sulfur bed content influences only the evaporation factor, because the variation of the initial bed properties affects the sulfur evaporation factor increases. Consequently, the sulfur evaporation factor increases.
Chapter 7: Modeling the Sulfur Release in the Inlet of the Rotary Kiln

initial sulfur, but the sulfur released is the same since the volatiles are the limited reactant. The modification of the fill degree does not influence the total SO$_2$ release, as shown in Figure 7-13, graph b). It can be seen that applying the same variation in an input parameter, the deviation is not the same for the positive and the negative variation, for example, a $+25\%$ variation on the mass particle deviates more from the reference results than the same negative variation.

<table>
<thead>
<tr>
<th>Input parameters</th>
<th>Variation +/-25%</th>
<th>Change in output variables</th>
<th>Deviation [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total SO$_2$ [g]</td>
<td>12.5</td>
<td>56.71 2.76 799.2</td>
<td>-0.56 3.33 4.58</td>
</tr>
<tr>
<td>Sulfur content [wt. %]</td>
<td>1.5</td>
<td>56.71 2.62 799.2</td>
<td>0.00 0.00 0.00</td>
</tr>
<tr>
<td>Fill degree [%]</td>
<td>7.5</td>
<td>56.71 2.69 1065</td>
<td>0.00 33.3 33.3</td>
</tr>
<tr>
<td>Degree of coverage [-]</td>
<td>0.525</td>
<td>42.54 2.07 598.5</td>
<td>-25.0 -25.3 25.0</td>
</tr>
<tr>
<td>Activation energy [kJ/mol]</td>
<td>108960</td>
<td>56.71 2.77 799.2</td>
<td>0.00 0.00 0.00</td>
</tr>
<tr>
<td>Pre-exponential factor [m/s]</td>
<td>1417.5</td>
<td>56.71 2.77 799.2</td>
<td>0.00 0.00 0.00</td>
</tr>
<tr>
<td>Firing degree [%]</td>
<td>7.5</td>
<td>40.83 1.99 575.5</td>
<td>-28.0 -28.2 -28.0</td>
</tr>
</tbody>
</table>

The actual uncertainty of the parameters may be higher than the +/-25\% variation depending on the operation control of a cement plant, for instance, the mass particle of fuels can have a wide range if the particle size is not screened, and the fuel degree of coverage will depend also on the mixing of the fuel with the raw materials. Furthermore, the uncertainty of the sulfur content in the bed material may also be higher if there is a significant circulation of sulfur, or it may be affected if the raw materials present significant inhomogeneities.

### 7.6 Model Evaluation

The rotary kiln model has been adapted to the pilot scale dimensions of the high temperature rotary drum in order to evaluate this model against the experimental data obtained in Chapter 6.

The model development, presented in section 7.4.3, is used with the dimensions for the high temperature rotary drum, which were specified in sections 5.2.1 and 6.2. The main difference between the rotary kiln model for...
an industrial case and the one adapted to the high temperature rotary drum is that the bed material consists of quartz sand and CaSO\textsubscript{4} and not of CaO surrounded by CaSO\textsubscript{4} as in the industrial case. The mean diameter of the used CaSO\textsubscript{4} is 6.49 μm with a specific surface area of 3.23 m\textsuperscript{2}/g. The analysis of the particle size is shown in Appendix E.

The axial length of rotary drum is 44 cm. The experimental results have shown that only a minor amount of CaSO\textsubscript{4} reacts, indicating that the reaction takes place in the proximity of the tube where the reducing agent is released. A finite length of the bed for the CSTR system, x, needs therefore to be defined in the model, where the reaction will take place only in this finite volume. Figure 7-16 illustrates the axial length rotary drum and for the CSTR.

Using 10 vol. % CO, different lengths of the bed material are considered for the CSTR in the model to investigate the effect of this parameter, as shown in Figure 7-17. The variation in the bed length affects the surface area of the CaSO\textsubscript{4} involved in the reaction (A\textsubscript{s} in equation 7.16), this means that not all CaSO\textsubscript{4} present in the bed material is accounted in the CSTR system. Consequently, the surface area needs to be scaled to the proportion of CaSO\textsubscript{4} in length of the bed, considering that the CaSO\textsubscript{4} is evenly distributed.
The predicted SO\(_2\) concentration decreases with increasing length of the bed, because the top area where the CO can diffuse out of the bed also increases and more CO can diffuse out. It may not be realistic to assume that the CO may diffuse in the axial direction and react with CaSO\(_4\) from a long distance of the injection. Therefore, the bed length of the CSTR is assumed to be 10 cm where the reaction takes place (5 cm in each side of the location of the tube). The surface area is thereby scaled to the proportion of CaSO\(_4\) in 10 cm of the bed. The model calculates the steady-state concentration of SO\(_2\) release when the CO is introduced. The modelling results are shown in Figure 7-18 together with the experimental results of SO\(_2\) concentration using different CO concentrations at 5 and 10 vol. % O\(_2\).

It can be seen that the modeling results follow the tendency of the experimental data, however the oxygen content in the freeboard atmosphere is not included in the mathematical model and it is assumed that the CO is well mixed. In the experiments, CO may not be a well-mixed in the bed and may be oxidized by the oxygen, which may diffuse to the bed, occupying the voids and causing a gradient of concentrations inside the bed. Furthermore, the adapted model has the uncertainty of the considered bed porosity and surface area of CaSO\(_4\), which may be different in the experiments because agglomeration of particles may also take place.

Figure 7-18: Comparison of the experimental results of SO\(_2\) concentration using different CO concentrations at 5 and 10 vol. % O\(_2\) and the modeling results.

The absolute level of the SO\(_2\) concentration cannot be predicted by the model since the bed length and the oxygen concentration are uncertain parameters. It can however be used for qualitative validation, i.e. to evaluate how a relative change in an input parameter affects the sulfur release. The percentage of SO\(_2\) release relative to the CO injected for the experimental data and for the modeling results are presented in Table 7-10 in order to compare how much CO has reacted.

Figure 7-18: Comparison of the experimental results of SO\(_2\) concentration using different CO concentrations at 5 and 10 vol. % O\(_2\) and the modeling results.

The absolute level of the SO\(_2\) concentration cannot be predicted by the model since the bed length and the oxygen concentration are uncertain parameters. It can however be used for qualitative validation, i.e. to evaluate how a relative change in an input parameter affects the sulfur release. The percentage of SO\(_2\) release relative to the CO injected for the experimental data and for the modeling results are presented in Table 7-10 in order to compare how much CO has reacted.
Table 7-10: Percentage of SO\(_2\) release relative to CO injected for different CO concentrations for the experimental and modelling results.

<table>
<thead>
<tr>
<th>CO conc. [vol. %]</th>
<th>SO(_2)/CO ratio [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>900 °C, 5 vol. % O(_2)</td>
<td>900 °C, 10 vol. % O(_2)</td>
</tr>
<tr>
<td>-------------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>5</td>
<td>2.02</td>
</tr>
<tr>
<td>7</td>
<td>2.74</td>
</tr>
<tr>
<td>10</td>
<td>6.67</td>
</tr>
<tr>
<td>15</td>
<td>13.2</td>
</tr>
<tr>
<td>20</td>
<td>16.1</td>
</tr>
</tbody>
</table>

The results for the model evaluation indicates that only a 6.07 % of CO reacts to form SO\(_2\), while for the rotary kiln model the CO was reacting almost 100 %. This is because in the rotary kiln model the CO that has not reacted is transferred to the next reactor increasing the probability of CO to react. For the evaluation of the adapted model only one CSTR is considered to calculate the steady-state concentration of SO\(_2\) release, because bed material is not moving in the axial direction.

Furthermore, to investigate in which scenario the model can fit the experimental data obtained at 10 vol. % O\(_2\), the fitting of the model results is performed varying the bed length and the degree of coverage. The results are shown in Figure 7-19. In this case, since there is no particle in either the model or the experiments, the degree of coverage influences the amount of CO that is in contact with the material bed. A length of 20 cm which is almost the half of the rotary drum is required. Varying the contact of CO with the material bed, the predicted SO\(_2\) concentration can be fitted at low concentrations of CO with 0.2 degree of coverage and at high CO concentrations with a degree of coverage of 0.5. The model was not able to simulate the experimental data obtained at 5 vol. % O\(_2\).

Figure 7-19: Model fitting to the experimental data obtained at 10 vol. % O\(_2\) varying the bed length and the degree of coverage.
Chapter 7: Modeling the Sulfur Release in the Inlet of the Rotary Kiln

In Chapter 6, it is mentioned that the SO$_2$ rate of formation could follow a first order expression, $\frac{d[SO_2]}{dt} = k(CO - C_{th})$, where $C_{th}$ is the threshold CO concentration which below this concentration no SO$_2$ is released. However, this is not implemented in the model because the kinetic constants for the reaction are developed for this case and it is believed that this threshold concentration may change depending on the sulfur content of the bed.

The validation of the kiln model is difficult to perform against industrial cement plant data because part of the SO$_2$ release may get absorbed and the measurement of SO$_2$ in the kiln inlet has some challenges, as will be explained in Chapter 9.

### 7.7 Conclusions

Modeling the behavior of rotary kilns is a complicated task involving heat transfer, gas-solid and solid-solid reactions, and particle mixing. In the literature, most of the models for rotary kilns are one-dimensional models for fossil fuels and are based on heat and mass transfer along the length of the kiln. More sophisticated physical three-dimensional models based on computational fluid dynamics have been also developed but are limited in their ability to model the clinker chemistry, bed motion, and thermodynamics. The different behavior between fossil and alternative fuels has encouraged the development of separate models for rotary kilns using alternative fuels.

A mathematical model which is able to predict sulfur release caused by volatiles from wood particles fired in the material kiln inlet has been developed in this chapter. The model is based on the reaction between the volatiles and CaSO$_4$ in the bed material, which is considered as continuous stirred tank reactors in series and therefore assuming well mixing between the volatile gases and the bed material.

SO$_2$ release was predicted when firing different wood particle mass substituting 10% of the energy required for production in the kiln inlet. The SO$_2$ released and consequently the sulfur evaporation factor increased with decreasing particle mass. The effect of the fuel degree of coverage, the bed fill degree, and the bed sulfur content was investigated for 25 wood particles of 10 g. The calculations showed that almost all CO reacts with CaSO$_4$ for the different cases. The total SO$_2$ release was the same for the different fill degrees, but the SO$_2$ concentration in the kiln inlet increased with increasing fill degree, because the material bed flow was decreased as well as the gas flow. For the different bed sulfur content, the same total SO$_2$ release and concentration in the kiln inlet was obtained because the limiting reactant was the volatiles, which was equal for the different cases. The sulfur evaporation factor increased with decreasing sulfur content in the bed and fill degree, while it decreased with increasing the fuel degree of coverage.

The modification of the firing degree was also studied considering wood particles of 10 g. The total SO$_2$ release and the sulfur evaporation factor increased with increasing firing degree in the kiln inlet. These model
predictions are in a good agreement with the experimental results from Chapter 5, except the effect of bed sulfur input. A sensitivity analysis have been applied to the kiln model in order to investigate the importance of the input parameters by evaluating the uncertainty in the outputs variables. By modifying one parameter at the time, the firing degree and the fuel degree of coverage were identified as the most influencing factors for the total SO2 release and the sulfur evaporation factor, while the kinetic parameters did not modify the output results.

The evaluation of the modeling results have been carried out by adapting the model to the high temperature rotary drum and comparing with the experimental results of Chapter 6. The modeling results follow the correct tendency of the experimental data, however, the absolute level of the SO2 concentration cannot be predicted by the model since the bed length and the oxygen concentration are uncertain parameters. The predictions of the kiln model can be used to evaluate how a relative change in an input parameter affects the sulfur release in a cement plant.

7.8 References

Chapter 7: Modeling the Sulfur Release in the Inlet of the Rotary Kiln


Chapter 7: Modeling the Sulfur Release in the Inlet of the Rotary Kiln


Chapter 7: Modeling the Sulfur Release in the Inlet of the Rotary Kiln


Chapter 7: Modeling the Sulfur Release in the Inlet of the Rotary Kiln


8. Model on Build-ups Tendency in the Kiln System

A model to predict the tendency of build-ups of a kiln system caused by sulfur and chlorine evaporation and condensation will be described in this chapter. The description of the system is explained in section 8.1, followed by the assumptions, and the model development. Two cases are considered; first when the kiln system operates with fuel in the calciner and kiln burner, and secondly, when the kiln system operates with alternative fuels substitution in the kiln inlet and the corresponding sulfur evaporation factor, calculated in Chapter 7, will be combined in this model.

8.1 Introduction

When partially converted or unburned alternative fuels drop into the material bed in the inlet of the rotary kiln, the sulfur may be released from the material bed contributing to a higher internal recirculation of sulfur. Deposit build-ups, which negatively affect the process stability of the kiln system, are a consequence of the internal recirculation of volatile constituents, as explained in Chapter 4.

The aim of the model of the build-up tendency in the kiln system is to predict the content of sulfur and chlorine in the hot meal, which is subsequently used to evaluate the risk of build-up formations in the calciner according to Figure 4-12 in Chapter 4.

The model is based on a mass balance of sulfur and chlorine around the preheater tower and the calciner. The input sources of sulfur and chlorine are the raw meal, and the fuel fired in the calciner and in the kiln burner. In the burning zone of the kiln, chlorine and sulfur evaporation from the raw materials takes place due to thermal degradation. The fraction evaporated and the input from the kiln burner can partly be absorbed in the kiln and the remaining part is absorbed in the calciner by fresh raw meal. Then the concentrations of SO$_3$ and Cl in the hot meal are calculated which re-enters the rotary kiln and the calculation steps are repeated until these concentrations do not change from iteration to iteration, reaching a steady-state. When considering alternative fuel substitution in the kiln inlet, sulfur evaporation takes place both in the kiln inlet due to reducing conditions and in the burning zone due to thermal decomposition.

The input and output solid mass flows in the kiln system are specified in Figure 8-1. The solid mass flows can be from raw material (black), dust transported with the gas flow (red), and fuel ashes (green) that can be incorporated in the material.
In order to simplify the mass flow system, it is assumed that the sulfur and chlorine of the fuel is included in the model as inputs to the gas phase. Furthermore, the mass contribution of the dust from the tertiary air is already included in the calculations of the hot meal mass flow. A simple scheme of the considered model system with the gas and solid flows is therefore illustrated in Figure 8-2, where the control volume of the model is indicated by the green dotted line.

Figure 8-2: Simplified scheme of the kiln system with the gas and solid flows and the concentrations of S and Cl that enters and exist the system. The boundaries of model are indicated by the green dotted line.
8.2 Kiln System without Alternative Fuel Substitution in the Kiln Inlet

8.2.1 Model Development

The model can be schematically summarized in different steps, as illustrated in Figure 8-3.

![Diagram of model development steps](image)

Figure 8-3: Scheme of the modeling steps for determining the SO$_3$ and Cl concentrations in the hot meal when the kiln system does not have alternative fuel substitution in the kiln inlet.

The input sulfur and chlorine concentrations of the raw meal are recalculated on basis of loss on ignition (LOI) free according to equation 8.1. The weight fraction on basis of loss of ignition free, $w_{j,\text{LOI free raw mat}}$, allows their comparison at different locations, after and before calcination.

\[
/w_{j,\text{LOI free raw mat}} = \frac{w_{j,\text{raw mat}}}{100 - \text{LOI}_{\text{raw mat}}} \quad \text{where } j = \text{S or Cl} \quad [8.1]
\]

where $w_{j,\text{raw mat}}$ is the sulfur or chlorine concentration in the raw meal in wt. %, and LOI$_{\text{raw mat}}$ is the percentage of loss on ignition of the raw meal.

It is considered that a fraction of the sulfur present in the raw meal leaves the preheater tower and is emitted through the stack. In a preheater kiln, it has been estimated that SO$_2$ emissions from the stack will count 15-30 % of the sulfur entering with the raw materials in the form of non-sulfates, i.e. pyrite and organic sulfur (Nielsen and Jepsen, 1990). Chlorine can also be released in the stack as HCl, however, due to a lack of reported values in the literature a fraction of 10 % of the chlorine entering with the raw materials is assumed.

The total sulfur and chlorine input, $\dot{m}_{\text{S,raw mat}}$ and $\dot{m}_{\text{Cl,raw mat}}$, from the raw materials and calciner fuel are determined, by equations 8.2 and 8.3, taking into account the respective mass flows and the fractions that leaves the preheater tower as SO$_2$ or HCl.
Chapter 8: Model on Build-ups Tendency in the Kiln System

\[ \mu_{\text{calciner}} = \mu_{\text{calciner, LOI free}} \left( \frac{W_{\text{calciner, LOI free}} (1 - \gamma_1)}{100} + \mu_{\text{fuel}} \right) \]  
\[ \mu_{\text{burner}} = \mu_{\text{burner, LOI free}} \left( \frac{W_{\text{burner, LOI free}} (1 - \gamma_1)}{100} + \mu_{\text{fuel}} \right) \]  

where \( W_{\text{calciner}} \) and \( W_{\text{burner}} \) are the sulfur and content of the calciner fuel in wt. %, respectively, \( \mu_{\text{calciner, LOI free}} \) is the net mass flow of the raw meal LOI free when introduced in the preheater in kg/h, \( \mu_{\text{burner, LOI free}} \) is mass flow of the fuel introduced into the calciner in kg/h, and \( \gamma_1 \) and \( \gamma_2 \) are the fraction of sulfur and chlorine, respectively, which leaves the preheater tower.

The net raw meal mass flow is calculated by the difference of the feed raw meal flow and the flow of dust loss out of the preheater. In order to this be valid, it is assumed that the same concentration of sulfur and chlorine that enters with the feed raw meal flow is the same in the flow of dust loss.

The recirculation of volatiles from the rotary kiln is included in the model by defining a sulfur evaporation factor, \( \epsilon_i \), a chlorine evaporation factor, \( \epsilon_i, Cl \), and a kiln sulfur absorption factor, \( \beta_i \). The iteration process starts by calculating the sulfur that evaporates in the kiln, \( \dot{n}_S, \text{burner} \), that enters the model system by the gas stream. For the first iteration \( (i = 1) \), the sulfur and chlorine molar flows correspond to the raw meal and for the following iterations \( (i \geq 2) \), the molar flows correspond to the hot meal. This is mathematically expressed as following where \( i \) is the number of iterations and \( N \) is the total number of iterations.

For \( i = 1 \) \( \beta_0, \epsilon_0 \equiv \beta_0, \epsilon_0, \text{raw meal} \equiv \beta_0, \epsilon_0, \text{feed input} \) and \( \beta_0 = \beta_0, \text{initial} \)

For \( i \geq 2 \) to \( N \) \( \beta_i, \epsilon_i \equiv \beta_i, \epsilon_i, \text{raw meal} \equiv \beta_i, \epsilon_i, \text{feed input} \) and \( \beta_i = \beta_i, \text{initial} \)

The sulfur that evaporates in the burning zone is calculated according to equation 8.4 by taking into account the sulfur evaporation factor, the sulfur input from the kiln burner fuel, \( \dot{n}_S, \text{burner} \), which is calculated by the sulfur content and the mass flow of the fuel, and the sulfur absorption of fuel.

\[ \dot{n}_{S, \text{evap}} = \left( \dot{n}_{S, \text{burner}} + \epsilon_i \cdot \dot{n}_S, \text{hot meal} \right) \left( 1 - \beta_i \right) \quad \text{for } i = 1 \text{ to } N \]  

For chlorine, it is assumed that there is no absorption in the kiln inlet due to its high volatility, however, this phenomena has not been reported and may be difficult to quantify as due to the inaccessibility of the rotary kiln during operation. The chlorine that evaporates is thereby determined by equation 8.5.

\[ \dot{n}_{Cl, \text{evap}} = \dot{n}_{Cl, \text{burner}} \left( 1 - \beta_i \right) \quad \text{for } i = 1 \text{ to } N \]  

In the calciner, the sulfur in the kiln gas stream is fully absorbed by fresh calcined raw meal (Rasmussen, 2011), and the chlorine fully condenses in the fresh calcined raw meal (Jøns et al., 2008). The fresh calcined
raw meal refers to raw meal that contains the total input of sulfur and chlorine from the raw materials and calciner fuel. Subsequently, the molar concentration of sulfur and chlorine in the hot meal (for \( i > 2 \)) can be calculated by equation 8.6 and 8.7.

\[
\dot{\chi}_{s,i} = \Dot{\chi}_{S,\text{feed}} + \Dot{\chi}_{S,\text{evap}} \\
\dot{\chi}_{c,i} = \dot{\chi}_{C,\text{feed}} + \dot{\chi}_{C,\text{evap}}
\]

for \( i = 1 \) to \( N \) \hspace{1cm} \text{(8.6)}

Then, the iteration process will continue by recalculating the \( \dot{\chi}_{S,\text{feed}} \) and \( \dot{\chi}_{C,\text{feed}} \) (equation 8.4 and 8.5) followed by determining a new molar concentration of sulfur and chlorine in the hot meal (equation 8.6 and 8.7). When this sulfur and chlorine concentration in the hot meal do not change from iteration to iteration, the system has reached steady-state and hot meal concentrations are determined by converting into mass flows multiplying by the molar mass of \( SO_3 \) and \( Cl \), respectively.

Finally, the \( SO_3 \) and \( Cl \) concentrations in the hot meal, \( w_{SO_3,\text{hot meal}} \text{ LOI free} \) and \( w_{Cl,\text{hot meal}} \text{ LOI free} \), are the molar flows of \( SO_3 \) and \( Cl \) in the hot meal in kg/h, \( \dot{\chi}_{\text{hot meal}} \) is the mass flow of the hot meal in the bottom cyclone in kg/h, and \( \text{LOI}_{\text{hot meal}} \) is the percentage of loss on ignition of the hot meal. Finally, the tendency of build-ups can be evaluated by using these concentrations.

The effect of chlorine removal by a bypass can also be included in the model by including a calculation step. The bypass, as mentioned in Chapter 4, is installed with the main purpose to remove chlorine, however, \( SO_3 \) may also be extracted with the kiln gases removed. Assuming a uniform concentration of the gas phase, the model also includes that the sulfur as \( SO_3 \) is removed by the bypass. The sulfur and chlorine that evaporate, calculated by equation 8.7 and 8.8, respectively, are used to determine the chlorine that condenses and the sulfur that absorbs in the hot meal by equation 8.10 and 8.12, respectively. Taking into account that a gas fraction will be removed with a bypass, a bypass absorbed factor, \( \psi \), is defined, which is directly related to the bypass size that is normally specified as a percentage of the kiln gases removed. Subsequently, the sulfur and chlorine in the hot meal, calculated according to equations 8.11 and 8.13, expresses the chlorine condensation and the sulfur absorption in the hot meal. These steps are repeated in each iteration process to
Chapter 8: Model on Build-ups Tendency in the Kiln System

achieve the SO\textsubscript{3} and Cl concentration in the hot meal. When the system reaches steady-state, the SO\textsubscript{3} and Cl concentrations in the hot meal are determined by equation 8.8 and 8.9, respectively.

\[ \dot{\chi}_{\text{Cl,SO}_{3},i} = \dot{\chi}_{\text{Cl,evap},i} \cdot (1 - \phi) \quad \text{for } i = 1 \text{ to } N \]  \hspace{1cm} [8.10]

\[ \dot{\chi}_{\text{Cl,SO}_{3},i} = \dot{\chi}_{\text{Cl,cond},i} + \dot{\chi}_{\text{Cl,abs},i} \quad \text{for } i = 1 \text{ to } N \]  \hspace{1cm} [8.11]

\[ \dot{\chi}_{\text{Cl,SO}_{3},i} = \dot{\chi}_{\text{Cl,evap},i} \cdot (1 - \phi) \quad \text{for } i = 1 \text{ to } N \]  \hspace{1cm} [8.12]

\[ \dot{\chi}_{\text{Cl,SO}_{3},i} = \dot{\chi}_{\text{Cl,cond},i} + \dot{\chi}_{\text{Cl,abs},i} \quad \text{for } i = 1 \text{ to } N \]  \hspace{1cm} [8.13]

8.2.2 Results

A cement plant with a clinker production of 3500 tons per day with an energy consumption of 2.993 MJ/kg clinker is considered the base for the calculations. The input parameters used for the model are specified in Table 8-1. The sulfur and chlorine content in the calciner and kiln burner fuel is typical for a low sulfur petroleum; however, it could also represent another fuel.

The fuel flows in the calciner and in the kiln burner, in kg/h, are determined by the energy required in each place, which is 60% in the calciner and 40% in the kiln burner, and the lower heating value of the fuel. The raw materials and hot meal flow and loss of ignition are chosen to be typical values in the cement industry; however, these values can vary depending on the type and origin of the different raw materials.

The sulfur and chlorine inputs in the raw materials are the recommended upper limits to introduce in the kiln system. The sources specify these limits are normally specified in loss of ignition free based, but these values have been converted to use as defined in this model.

The sulfur and the chlorine evaporation factors can vary between 0.3 and 0.7 and from 0.90 to 0.99, respectively, as previously mentioned in Chapter 4. The values of these parameters have been assumed in their typical range, however, the parameters depend significantly on other process variables, such as temperature in the burning zone and oxygen content in the kiln and this is not considered in the present model.

In order to check the mass balance, the mass flows of the raw meal and hot meal are calculated in loss of ignition free based, which allows their comparison at different locations, after and before calcination. In Figure F-1 in Appendix F, the typical material feed, hot meal and dust loss are specified.
The output of the model is the predicted SO$_2$ and Cl content in the hot meal. For the parameters in Table 8-1, the SO$_2$ and Cl content are 2.45 and 0.83 wt. %, respectively. Figure 8-4 shows the result obtained, indicated by a blue cross in the diagram for predicting the tendency of build-ups. Furthermore, when the bypass absorbed factor is introduced for a new calculation, the chlorine condensation and the sulfur absorption in the calciner are reduced as illustrated by a red star in Figure 8-4. With bypass, the SO$_2$ and Cl concentrations in the hot meal obtained are 1.98 and 0.19 wt. %, respectively.
According to the definitions of the zones in the graph, the cement plan without bypass will have a medium tendency of build-up and with bypass a medium build-up tendency, quite close to the low tendency area.

A sensitivity analysis of the individual parameters has been carried out in order to investigate the effect of the parameters on the SO$_3$ and Cl content of the hot meal. The sulfur and chlorine input concentrations and evaporation factors have been investigated. Each input parameter is changed with +/- 25% while keeping the remaining parameters constant, except for the chlorine evaporation, which has tested for the interval limits of its variation. Table 8-2 summarizes the variation input values and the output results obtained in each case specifying SO$_3$ and Cl concentration in hot meal and in which zone of the build-up tendency diagram that scenario belongs. Furthermore, the deviation from the output results obtained by the initial case is determined in order to evaluate the influence of the parameter.

The results show that chlorine evaporation factor has the largest influence on the output variables with 400% deviation on the Cl concentration compared to the reference case when the chlorine evaporation factor was 0.99. The variation of the sulfur evaporation factor greatly influences the SO$_3$ concentration with -23% and 42% deviation when the input is varied +/- 25%. The ranking is followed by the sulfur concentration in the calciner fuel (with almost +/- 14% deviation) and in the kiln burner (with +/- 8% deviation). On the contrary, the chlorine input in the calciner fuel and the sulfur content in the raw materials content do not influence significantly to output results. The bypass reduces significantly the chlorine circulation even when the chlorine evaporation factor is maximum. The actual uncertainty of the sulfur and chlorine in the fuels may be higher than +/- 25% variation, depending on the homogeneity of the used fuel. The uncertainty of the sulfur and...
the steps needed to determine the SO$_3$ evolution during the kiln system operation. When alternative fuels are fired in the kiln inlet, sulfur evaporation also takes place in the kiln inlet and thereby the steps needed to determine the SO$_3$ concentration in the hot meal can be summarized in Figure 8-5. The model steps for the calculation of the CI concentration in the hot meal are not modified, since the chlorine is not affected by the combustion of alternative fuels in contact with the kiln bed material.

### 8.3 Kiln System with Alternative Fuel Substitution in the Kiln Inlet

#### 8.3.1 Model Modification

When alternative fuels are fired in the kiln inlet, sulfur evaporation also takes place in the kiln inlet and thereby the steps needed to determine the SO$_3$ concentration in the hot meal can be summarized in Figure 8-5. The model steps for the calculation of the CI concentration in the hot meal are not modified, since the chlorine is not affected by the combustion of alternative fuels in contact with the kiln bed material.
The total sulfur from the raw materials and fuel are determined using the same procedure explained in section 8.2.1 (equations 8.1, and 8.2). Due to alternative fuels firing in the kiln inlet, the sulfur evaporation at the kiln inlet, $\delta S_{\text{evap kiln inlet}}$, is described for each iteration according to equation 8.14, where $\delta S_{\text{evap kiln inlet}}$ is the sulfur evaporation factor in the kiln inlet obtained in Chapter 7. The sulfur evaporated in the kiln inlet is assumed that cannot be absorbed along the rotary kiln because the gas will flow towards the calciner.

\[ \delta S_{\text{evap kiln inlet}} = \delta S_{\text{inlet}} \times S_{\text{inlet}} \] \[ \text{for } i = 1 \text{ to } N \] \[ [8.14] \]

The remaining sulfur in the solid bed material inside the rotary kiln, $\delta S_{\text{remaining}}$, is calculated by the difference of the sulfur input in the raw meal ($i = 1$) or hot meal ($i > 2$) and the sulfur evaporated in the kiln inlet (equation 8.15).

\[ \delta S_{\text{remaining}} = \delta S_{\text{input}} - \delta S_{\text{evap kiln inlet}} \] \[ \text{for } i = 1 \text{ to } N \] \[ [8.15] \]

The remaining sulfur can evaporate in the burning zone of the rotary kiln and the sulfur from the kiln burner fuel also contributes to the gas phase $SO_3$. The sulfur evaporated in the burning zone may also be absorbed along the kiln. Therefore, the sulfur evaporation at the burning zone, $\delta S_{\text{evap calciner}}$, is mathematically determined by equation 8.16.

\[ \delta S_{\text{evap calciner}} = \delta S_{\text{input}} - \delta S_{\text{remaining}} \] \[ \text{for } i = 1 \text{ to } N \] \[ [8.16] \]

The remaining sulfur in the solid bed material inside the rotary kiln, $\delta S_{\text{remaining}}$, is described for each iteration according to equation 8.14, where $\delta S_{\text{remaining}}$ is the sulfur evaporation factor in the kiln inlet obtained in Chapter 7. The sulfur evaporated in the kiln inlet is assumed that cannot be absorbed along the rotary kiln because the gas will flow towards the calciner.

\[ \delta S_{\text{evap kiln inlet}} = \delta S_{\text{inlet}} \times S_{\text{inlet}} \] \[ \text{for } i = 1 \text{ to } N \] \[ [8.14] \]

The remaining sulfur can evaporate in the burning zone of the rotary kiln and the sulfur from the kiln burner fuel also contributes to the gas phase $SO_3$. The sulfur evaporated in the burning zone may also be absorbed along the kiln. Therefore, the sulfur evaporation at the burning zone, $\delta S_{\text{evap calciner}}$, is mathematically determined by equation 8.16.
Chapter 8: Model on Build-ups Tendency in the Kiln System

\[ \dot{h}_{\text{evap, end, } i} = \dot{h}_{\text{evap, inlet, } i} + \dot{h}_{\text{rec, end, } i} + \dot{h}_{\text{rec, inlet, } i} \quad \text{for } i = 1 \text{ to } N \quad [8.16] \]

The sulfur in the hot meal can finally be determined by equation 8.17. Then, equations 8.14, 8.15, 8.16, and 8.17 are recalculated until the system reach steady-state by reaching a stable value of the sulfur molar flow.

\[ \dot{h}_{\text{evap, end, } i} = \dot{h}_{\text{evap, inlet, } i} + \dot{h}_{\text{rec, end, } i} + \dot{h}_{\text{rec, inlet, } i} \quad \text{for } i = 1 \text{ to } N \quad [8.17] \]

A large number of iterations are needed to reach a stable sulfur concentration in the hot meal since the sulfur recirculation is increased significantly in the initial iterations.

8.3.2 Results

It is considered that 10 % of the energy required for cement production from the calciner is substituted fuel fired in the kiln inlet. The fuel used consist of wood particles of 1 g each, which does not contain neither sulfur nor chlorine. In Chapter 7, a sulfur evaporation factor of 0.04 was obtained for this scenario. Using the initial input parameters specified in Table 8-1 and the sulfur evaporation factor in the kiln inlet, the SO\(_3\) and Cl concentrations in the hot meal are 2.55 and 0.83 wt. %, respectively. A cement plant operating under these conditions will experience a high build-up tendency, as shown in Figure 8-6.

When firing alternative fuels in the kiln inlet, the calciner fuel flow is typically reduced in order to avoid too high calciner temperature. Then, a 10 % of the calciner fuel flow is reduced, from 8725.4 kg/h to 7852.8 kg/h, and the SO\(_3\) and Cl concentrations in the hot meal correspond to 2.41 and 0.83 wt. %, respectively.

Introducing the bypass absorbed chlorine factor, \(\varphi=0.15\) and using 7852.8 kg/h calciner fuel, the SO\(_3\) and Cl concentrations in the hot meal obtained are 1.94 wt. % and 0.19 wt. %, respectively. Figure 8-6 shows that the results of these scenarios are in the medium tendency zone in the diagram of build-up tendency.
A sensitivity analysis of the SO$_3$ and Cl content of the hot meal, when the calciner fuel flow is reduced 10% (7852.8 kg/h), is conducted using the same procedure as in section 8.2.2 by changing one parameter at the time with +/- 25% and compare it with the initial case. However, only the sulfur input parameters are studied since the alternative fuels firing in the kiln inlet does not modify the chlorine cycle.

A sensitivity analysis of the SO$_3$ and Cl content in the hot meal (without bypass) plus firing alternative fuels in the kiln inlet causing a sulfur evaporation factor of 0.04, when the calciner fuel flow is reduced 10% and when bypass is included.

The sensitivity analysis show that the sulfur evaporation factor at the burning zone is the most influencing parameter to the SO$_3$ concentration in the hot meal with a -23% and 41% deviation to the reference case when the input is changed +/- 25% of its value. The ranking is followed by the sulfur input in the calciner fuel (with

The sensitivity analysis show that the sulfur evaporation factor at the burning zone is the most influencing parameter to the SO$_3$ concentration in the hot meal with a -23% and 41% deviation to the reference case when the input is changed +/- 25% of its value. The ranking is followed by the sulfur input in the calciner fuel (with
Chapter 8: Model on Build-ups Tendency in the Kiln System

+/- 13 % deviation) and in the kiln burner fuel (with almost +/- 9 % deviation). The variation of the kiln inlet sulfur evaporation factor does not give a significant variation in the SO\textsubscript{3} in the hot meal. However, the actual uncertainty of this input parameter may depend on the fuel type, particle size and degree of coverage and may contributed with higher kiln inlet sulfur evaporation factor value.

8.4 Model Limitations

The model developed for prediction of the build-up tendency in the kiln system does not consider the interaction of alkali with sulfur and chlorine, which may influence the volatile cycles.

The dust recirculation in the preheater tower and the efficiency of each cyclone are taken into account indirectly by the material flows in the inlet and outlet of the preheater tower. Furthermore, the sulfur and chlorine content in the dust may be different than in the material flow in each cyclone stage, and this effect is not included in the model.

The model does not included that the alternative fuel fired in the kiln inlet contributes with sulfur and chlorine inputs. These contributions may need to be further implemented because many of alternative fuels contain sulfur and/or chlorine, as showed in Table 3-2. Furthermore, it was assumed that the mass flow and that the sulfur and chlorine in the calciner and burner fuels are inputs to the gas phase, and thereby the fuel ash is not accounted in the mass balance. To use a solid fuel in the model, it is necessary to take into account the fuel ash contribution to the hot meal flow and subsequently to the clinker. However, this limitation will not influence so much the model results because if it is assumed that the used calciner fuel has 0.5 wt. % ash, the ash mass will contribute to 4362.5 kg/h, which is a 2.92 % of the raw material flow.

The model does not determine either the clinker quality in respect to SO\textsubscript{3} and Cl or the emissions in stack or bypass, because the gas flow is normally used in the mill and it is out of the purpose of this model.

8.5 Conclusions

A model to predict the tendency of build-ups of a kiln system based on the SO\textsubscript{3} and Cl concentrations in the hot meal has been developed. The model gives realistic results because the output concentrations are in the range expected.

Results are obtained specifying the sulfur and chlorine content in the raw material and calciner fuel, and the sulfur and chlorine evaporation factors. For a cement plant with 3500 tons per day without bypass using raw materials with 0.05 wt. % S and 0.01 wt. % Cl and fuel with 5 wt. % S and 0.001 wt. % Cl, the tendency of build-ups predicted was in the medium/high line, while using bypass the tendency of build-ups was medium, close to the low region. A sensitivity analysis was performed in order to investigate the effect of the parameters on the SO\textsubscript{3} and Cl content of the hot meal and showed that the chlorine evaporation factor has the largest contribution to the hot meal flow and subsequently to the clinker. However, this limitation will not influence so much the model results because if it is assumed that the used calciner fuel has 0.5 wt. % ash, the ash mass will contribute to 4362.5 kg/h, which is a 2.92 % of the raw material flow.

The model does not determine either the clinker quality in respect to SO\textsubscript{3} and Cl or the emissions in stack or bypass, because the gas flow is normally used in the mill and it is out of the purpose of this model.

Chapter 8: Model on Build-ups Tendency in the Kiln System

8.4 Model Limitations

The model developed for prediction of the build-up tendency in the kiln system does not consider the interaction of alkali with sulfur and chlorine, which may influence the volatile cycles.

The dust recirculation in the preheater tower and the efficiency of each cyclone are taken into account indirectly by the material flows in the inlet and outlet of the preheater tower. Furthermore, the sulfur and chlorine content in the dust may be different than in the material flow in each cyclone stage, and this effect is not included in the model.

The model does not included that the alternative fuel fired in the kiln inlet contributes with sulfur and chlorine inputs. These contributions may need to be further implemented because many of alternative fuels contain sulfur and/or chlorine, as showed in Table 3-2. Furthermore, it was assumed that the mass flow and that the sulfur and chlorine in the calciner and burner fuels are inputs to the gas phase, and thereby the fuel ash is not accounted in the mass balance. To use a solid fuel in the model, it is necessary to take into account the fuel ash contribution to the hot meal flow and subsequently to the clinker. However, this limitation will not influence so much the model results because if it is assumed that the used calciner fuel has 0.5 wt. % ash, the ash mass will contribute to 4362.5 kg/h, which is a 2.92 % of the raw material flow.

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8.5 Conclusions

A model to predict the tendency of build-ups of a kiln system based on the SO\textsubscript{3} and Cl concentrations in the hot meal has been developed. The model gives realistic results because the output concentrations are in the range expected.

Results are obtained specifying the sulfur and chlorine content in the raw material and calciner fuel, and the sulfur and chlorine evaporation factors. For a cement plant with 3500 tons per day without bypass using raw materials with 0.05 wt. % S and 0.01 wt. % Cl and fuel with 5 wt. % S and 0.001 wt. % Cl, the tendency of build-ups predicted was in the medium/high line, while using bypass the tendency of build-ups was medium, close to the low region. A sensitivity analysis was performed in order to investigate the effect of the parameters on the SO\textsubscript{3} and Cl content of the hot meal and showed that the chlorine evaporation factor has the largest
influence with almost 400% deviation on the Cl concentration when the evaporation factor was 0.99 as opposed to the reference case of 0.95. On the contrary, the modification on the chlorine content in the calciner fuel did not vary the output results and sulfur content in the raw material influenced only with ±/−4% deviation at a 25% input variation.

When alternative fuels are fired in the kiln inlet, sulfur evaporation at the kiln inlet is taken into account as well as the sulfur evaporation at the burning zone. The results showed that the plant will experience medium tendency build-ups, except when operating with bypass. The sensitivity analysis results show that the sulfur evaporation factor at the burning zone is the most influencing parameter to the SO₂ concentration in the hot meal with a -23% and 41% deviation at an input variation of 25%, while the variation of the kiln inlet sulfur evaporation factor has a small effect on the output.

When the bypass chlorine absorption factor is considered in the model, the chlorine concentration in the hot meal is significantly reduced both with and without firing alternative fuels in the kiln inlet.

The model is limited by not taking the alkali interaction, dust recirculation in the preheater tower, and the sulfur and chlorine input from the fuel fired in the kiln inlet into account.

### 8.6 References


9. Industrial Experience on Sulfur Release

The purpose of this chapter is to study the sulfur release in the kiln inlet on an industrial plant, which fires alternative fuels in the calciner and the kiln riser.

The aim of the industrial study was to investigate the relationship between organic carbon in the last cyclone (bottom stage cyclone) and SO$_2$ in the gas phase in the kiln inlet, because the organic carbon from the hot meal is believed to be directly related to unburned calciner fuel. Unburned light fuel particles can be carried upwards with the gas flow through the calciner and transported into the bottom stage cyclone. The char particles may arrive to the kiln inlet and their subsequent combustion may cause the release of sulfur.

The investigation was carried out by analysis of hot meal samples and process data from an industrial cement plant. Multicomponent gas measurements were compared with the stationary measurement equipment of the cement plant in order to support the investigations of sulfur release during combustion in the kiln inlet.

The chapter starts with a description of the plant, such as the system design, the fuels used, and a description of the tests performed. Section 9.2 describes the two gas measurements systems used in the kiln inlet and compares their results. The investigation of sulfur evaporation from the process is explained in section 9.3, which includes the organic carbon results from the hot meal samples and analyses of the calciner fuel conversion, the tendency of build-ups, and the sulfur volatility. Finally, the conclusions of the industrial experience and the challenges encountered in the sulfur release study are described.

9.1 Background

The cement plant, where the investigation was carried out, has two separate line calciners. The strings, named string A and B, are identical and consist of a calciner and three cyclones, as shown schematically in Figure 9-1. The raw materials used are wet and form a slurry, which is introduced into the dryer crusher of each stream where the slurry is dried and ground. The dry raw materials are then carried upwards to the top cyclone by the gas stream. The gases in the preheater tower are bypassed from the second cyclone to the dryer crusher before going to the top cyclone, which works as gas/dust separator. The hot air from the clinker cooler goes to the calciner and the rotary kiln gases are mixed with the calciner outlet gases. The plant produces mineralized clinker, which means that 0.13 wt. % fluoride on clinker basis is added in the kiln inlet, which allows lowering the burning temperature in the kiln.
The fuels used in both calciners are petcoke and plastic/paper-based refused derived fuel (RDF). Sometimes, tire chips are fired in the riser duct from 2 meters above the kiln inlet. The fuel analyses of petcoke, RDF, and tire chips are specified in Table 9-1, where a.r. denotes as received.

Table 9-1: Fuel analyses and lower heating values (LHV) of petcoke, RDF, and tire chips that the cement plant used in the calciner and riser duct. Notes: 1 Volatile matter, 2 Fixed carbon.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Moisture [wt. % a.r.]</th>
<th>Proximate analysis [wt. % a.r.]</th>
<th>Ultimate analysis [wt. % a.r.]</th>
<th>LHV [MJ/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>VM¹</td>
<td>FC²</td>
<td>Ash</td>
</tr>
<tr>
<td>Petcoke</td>
<td>1.1</td>
<td>13.0</td>
<td>84.9</td>
<td>1.0</td>
</tr>
<tr>
<td>RDF</td>
<td>24.1</td>
<td>61.6</td>
<td>6.6</td>
<td>7.7</td>
</tr>
<tr>
<td>Tire chips</td>
<td>-</td>
<td>64</td>
<td>3.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Figure 9-1: Scheme of the industrial cement plant where the investigation took place. Not to scale.

The fuels used in both calciners are petcoke and plastic/paper-based refused derived fuel (RDF). Sometimes, tire chips are fired in the riser duct from 2 meters above the kiln inlet. The fuel analyses of petcoke, RDF, and tire chips are specified in Table 9-1, where a.r. denotes as received.

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<th>Fuel</th>
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<th>Proximate analysis [wt. % a.r.]</th>
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<th>LHV [MJ/kg]</th>
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<tr>
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<td>24.1</td>
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<td>7.7</td>
</tr>
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<td>Tire chips</td>
<td>-</td>
<td>64</td>
<td>3.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>
The cement plant controls the calciner temperature by adjusting the flow of petcoke fired. In order to estimate the amount of RDF fired, the percentage of fuel input to each calciner originating from petcoke is calculated by to equation 9.1. The percentage remaining of fuel input corresponds to RDF:

\[ \text{petcoke}\% = \frac{F_{\text{petcoke}} \cdot \text{LHV}_{\text{petcoke}}}{E_{\text{calc}}} \cdot 100 \]  

where \( F_{\text{petcoke}} \) is the flow of petcoke in t/h fired into the calciner, \( \text{LHV}_{\text{petcoke}} \) is the lower heating value of the petcoke, which is approx. 33.5 \( \cdot 10^6 \) J/kg (the lower heating value for petcoke is 35.183 \( \cdot 10^6 \) J/kg according to the analysis, but the fired petcoke is mixed with unspecified fuels), \( E_{\text{calc}} \) is the energy consumption of the calciner, which is estimated to be 29.3 \( \cdot 10^5 \) J/kg clinker, and \( F_{\text{produc}} \) is the production of each string in t/h.

The tire chips are assumed not to contribute to the calciner energy consumption, because the amount of fuel fired in the main burner is reduced when tire chips are fired. Figure 9-2 qualitatively illustrates the flows of mixture fuel fired in the main burner and tire chips. The temperature in the hot zone can be lowered, because the gas temperature in the kiln inlet will increase due to the combustion of tire chips. The tire chips fired in the kiln inlet contribute therefore to the energy consumption of the main burner. The fuel in the main burner consists of a mixture of 50 wt. % steam coal and 50 wt. % low sulfur petcoke, and the overall sulfur content in the mixture is 2.7 wt. %.

Hot meal samples were taken from the bottom cyclone of strings A and B during a period of one month in 8 different sampling days. The hot meal samples were taken with a sampler provided by FLSmidth A/S to ensure a homogenous cooling and to avoid oxidation of the carbon. Multicomponent gas measurements with focus on...
SO₂, CO, and O₂ in the kiln inlet were performed on sampling day 3 and 4 using a hot Fourier transform infrared spectroscopy (FTIR) measurement system with a heated self-cleaning probe and samples were also taken during these days.

The two tests performed consisted of:
- Test 1: Increase of RDF firing in calciner A (from 37 to 85 % RDF of calciner fuel input). Petcoke flow was decreased from 4.6 to 1.1 t/h. No tire chips were fired in the kiln inlet.
- Test 2: Increase of tire chips injection in the kiln inlet from 1 to 1.5 t/h.

9.2 Gas Measurements

During the visit to the cement plant, a hot FTIR gas measurement system was used and compared to a cold gas measurement system, typically used in the cement industry. The main difference between the systems is that the hot FTIR system measures the components in the analyzer using the hot gases, while the fixed installation of the plant (cold gas system) needs to cool the gas before the measurement. The cooling of the gas can affect the measurements because condensed moisture can absorb SO₂. The measurement principle of both techniques can be found in Appendix G.

9.2.1 Comparison between Two Measurements Systems

The fixed equipment (the cold gas measuring system) logs the data every 60 seconds and purges the probe (to remove the dust that may enter) every 10 minutes. The FTIR equipment was set to log data every 5 seconds, and a self-purge cleaning mechanism was set up to purge every 5 minutes. Therefore, the FTIR equipment was sampling more frequently and it was also cleaned more frequently in order to avoid the SO₂ absorption. Furthermore, the detection limits of the FTIR system were lower than for the fixed equipment.

The probe used for the hot FTIR equipment had smaller dimensions than the one used for the fixed equipment. This was an advantage because the gas residence time in the probe and the filter was shorter than normal, which means, that the gases had less time to react or be absorbed inside the probe.

The FTIR equipment was placed on a level 3-4 meters above the fixed equipment. Therefore, the fixed equipment was measuring more directly into the kiln gases. Figure 9-3 illustrates representatively the location of the hot FTIR gas measurement system and the fixed cold gas measurement system in the kiln system.
Chapter 9: Industrial Experience on Sulfur Release

Figure 9-3: Scheme of the location of the hot FTIR gas measurement system and the fixed cold gas measurement system.

The FTIR equipment recorded concentrations of CO and SO\(_2\) when the fixed equipment showed lower concentrations than 0.02 vol. % of CO and 0 ppm SO\(_2\). The CO and SO\(_2\) spikes were observed in brief periods during test 1 and 2. It was noticed that the O\(_2\) levels measured by the FTIR equipment were at least 1 vol. % higher than the kiln inlet probe position from the fixed equipment.

The fixed gas analyzer recorded 0 ppm SO\(_2\) in the kiln inlet, even though the fuel mixture in the main burner has 2.7 wt. % of sulfur. Assuming that the fuel mixture has a composition of 86.9 wt. % C, 3.71 wt. % H, 3.15 wt. % N, and 2.7 wt. % S and that it is combusted in 6 vol. % O\(_2\) (which is the approximate level observed in Table 9-2), the SO\(_2\) concentration at the kiln inlet coming from main burner should be approx. 1400 ppm SO\(_2\) assuming no SO\(_2\) absorption by the dust or clinker. However, this high SO\(_2\) concentration is not seen in the kiln measurements, which means that the sulfur has been absorbed by the clinker or by the dust in the cement kiln.

Figure 9-4 and Figure 9-5 show the O\(_2\), CO, and SO\(_2\) measurements with the fixed equipment and the FTIR equipment for normal operation, test 1, and the addition of 1 t/h tire chips during the sampling day 3.

The CO measurements by the fixed equipment cannot be trusted because the uncertainty of this measurement is usually 2 % of the full range of the equipment, which is from 0 to 5 vol. % CO, therefore the uncertainty is ± 0.1 % CO.
Some spikes of CO and SO₂ were briefly observed with the FTIR equipment, while with the fixed equipment very small CO spikes were recorded and the SO₂ concentration did not change. Table 9-2 summarizes the averages, maximum and minimum concentrations of O₂, CO, and SO₂ during the different periods. The FTIR equipment measured 80 and 277 ppm as maximum concentration of CO and SO₂, respectively.

Table 9-2: Summary of the average (avg), maximum and minimum concentrations of O₂, CO, and SO₂ measured by the FTIR equipment and the fixed equipment during normal operation, test 1 and addition of tire chips.

<table>
<thead>
<tr>
<th>FTIR equipment</th>
<th>O₂ [vol. %]</th>
<th>CO [ppm]</th>
<th>SO₂ [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Production</td>
<td>avg</td>
<td>max</td>
<td>min</td>
</tr>
<tr>
<td>Test 1</td>
<td>6.8</td>
<td>8</td>
<td>5.6</td>
</tr>
<tr>
<td>Addition tire chips 1 t/h</td>
<td>7.1</td>
<td>8.3</td>
<td>5.7</td>
</tr>
<tr>
<td>Fixed equipment</td>
<td>O₂ [vol. %]</td>
<td>CO [ppm]</td>
<td>SO₂ [ppm]</td>
</tr>
<tr>
<td>----------------</td>
<td>-------------</td>
<td>----------</td>
<td>-----------</td>
</tr>
<tr>
<td>Normal Production</td>
<td>avg</td>
<td>max</td>
<td>min</td>
</tr>
<tr>
<td>Test 1</td>
<td>5.9</td>
<td>6.6</td>
<td>5.1</td>
</tr>
<tr>
<td>Addition tire chips 1 t/h</td>
<td>5.7</td>
<td>6.5</td>
<td>5.1</td>
</tr>
</tbody>
</table>

Figure 9-4: O₂, CO and SO₂ concentrations in the kiln inlet measured by the fixed equipment for normal operation, test 1 and the addition of tire chips (1 t/h). Probe cleaning effects have been removed.

Figure 9-5: O₂, CO and SO₂ concentrations in the kiln inlet measured by the FTIR equipment for normal operation, test 1 and the addition of tire chips (1 t/h). Probe cleaning effects have been removed.

Some spikes of CO and SO₂ were briefly observed with the FTIR equipment, while with the fixed equipment very small CO spikes were recorded and the SO₂ concentration did not change. Table 9-2 summarizes the averages, maximum and minimum concentrations of O₂, CO, and SO₂ during the different periods. The FTIR equipment measured 80 and 277 ppm as maximum concentration of CO and SO₂, respectively.

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<th>SO₂ [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Production</td>
<td>avg</td>
<td>max</td>
<td>min</td>
</tr>
<tr>
<td>Test 1</td>
<td>6.8</td>
<td>8</td>
<td>5.6</td>
</tr>
<tr>
<td>Addition tire chips 1 t/h</td>
<td>7.1</td>
<td>8.3</td>
<td>5.7</td>
</tr>
<tr>
<td>Fixed equipment</td>
<td>O₂ [vol. %]</td>
<td>CO [vol. %]</td>
<td>SO₂ [ppm]</td>
</tr>
<tr>
<td>----------------</td>
<td>-------------</td>
<td>-----------</td>
<td>-----------</td>
</tr>
<tr>
<td>Normal Production</td>
<td>avg</td>
<td>max</td>
<td>min</td>
</tr>
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<td>Test 1</td>
<td>5.9</td>
<td>6.6</td>
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</tr>
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<td>6.5</td>
<td>5.1</td>
</tr>
</tbody>
</table>

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Table 9-2: Summary of the average (avg), maximum and minimum concentrations of O₂, CO and SO₂ measured by the FTIR equipment and the fixed equipment during normal operation, test 1 and addition of tire chips.
Figure 9-6 shows an enlargement of the O\textsubscript{2}, CO, and SO\textsubscript{2} concentration profiles in the kiln inlet measured by the FTIR equipment during test 1. It can be seen that the O\textsubscript{2} concentration increases when the probe is purged. This means that no dust is present inside the probe, subsequently higher concentrations of SO\textsubscript{2} are measured, which is the SO\textsubscript{2} concentration present in the kiln inlet. Afterwards, the SO\textsubscript{2} concentration slowly decreases, because the SO\textsubscript{2} is absorbed in dust or/and on the probe filter. The O\textsubscript{2} concentration is around 6 vol. %, which is the level present in the kiln gas. This cycle is repeated for each purge.

It can be seen that the dust from the kiln constitute a challenge when measuring the “real” SO\textsubscript{2} concentration in the kiln.

Figure 9-7 and Figure 9-8 show the O\textsubscript{2}, CO, and SO\textsubscript{2} concentration profiles obtained with the fixed equipment and the FTIR equipment during normal operation and during test 2 at sampling day 4. When the tire chips were increased from 1 to 1.5 t/h, spikes of CO and SO\textsubscript{2} were only seen with the FTIR equipment.
In general, the SO₂ concentration levels were low and the spikes were brief, so the fixed installation had difficulties to measure the process changes which occurred so briefly. The purge function and sampling

The average concentrations, the maximum and minimum concentrations of O₂, CO and SO₂ for the measurements performed on day 4 are listed in Table 9-3. The maximum concentration of CO and SO₂ detected with the FTIR equipment were 1792 ppm and 233 ppm, respectively.

Table 9-3: Summary of the average (avg), maximum and minimum concentrations of O₂, CO and SO₂ measured by the FTIR equipment and the fixed equipment during normal operation and test 2.

<table>
<thead>
<tr>
<th>Measurements of Sampling day 4</th>
<th>O₂ [vol. %]</th>
<th>CO [ppm]</th>
<th>SO₂ [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTIR equipment</td>
<td>avg</td>
<td>max</td>
<td>min</td>
</tr>
<tr>
<td>Normal Production</td>
<td>7.4</td>
<td>8.5</td>
<td>5.5</td>
</tr>
<tr>
<td>Test 2</td>
<td>7.5</td>
<td>8.9</td>
<td>6</td>
</tr>
<tr>
<td>Normal Production</td>
<td>7.9</td>
<td>9.9</td>
<td>5.8</td>
</tr>
<tr>
<td>Fixed equipment</td>
<td>O₂ [vol. %]</td>
<td>CO [vol. %]</td>
<td>SO₂ [ppm]</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>-------------</td>
<td>----------</td>
<td>-----------</td>
</tr>
<tr>
<td>FTIR equipment</td>
<td>avg</td>
<td>max</td>
<td>min</td>
</tr>
<tr>
<td>Normal Production</td>
<td>6.5</td>
<td>8.7</td>
<td>4.3</td>
</tr>
<tr>
<td>Test 2</td>
<td>6.2</td>
<td>7.5</td>
<td>5.5</td>
</tr>
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<td>4.1</td>
</tr>
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In general, the SO₂ concentration levels were low and the spikes were brief, so the fixed installation had difficulties to measure the process changes which occurred so briefly. The purge function and sampling
conditioning of the FTIR equipment did improve the measurements, but the dust in the probe also quickly started to absorb SO$_2$.

In conclusion, there is a good agreement of the oxygen concentration levels measured by the two measurement equipments, but the hot FTIR gas measurement equipment is able to measure changes in CO and SO$_2$ concentrations that were not detected by the cold gas measurement equipment. The CO concentration measured by the cold gas measurement equipment cannot be trusted because the CO concentration levels are below the uncertainty. The SO$_2$ concentration cannot be either trusted because the data log and purge time is quite long, which makes that the analyzer is not detecting the fast variations. Furthermore, the lack of frequent maintenance (meaning that the dust in filters may not been removed) may have influence the results, obtaining no detection of SO$_2$.

9.3 Investigation of Sulfur Evaporation on the Process

Hot meal samples were taken from the bottom cyclone of strings A and B at 8 separate days during a month period. During this period, one sample from each calciner string was taken during normal operation, but on sampling days 5 and 6 only one sample was taken from B string because the A-string was out of operation. During the visit on sampling day 3 and 4, the following samples were taken:

- Sampling day 3: two samples during normal operation and three samples (two from string A and one from B) during a period where the RDF was increased in calciner A.
- Sampling day 4: two samples (one from string A and one from B) during a period with increased tire chips injection in the kiln inlet.

The samples were sent to the FLSmidth A/S laboratory for analyses of the chemical composition (by X-Ray diffraction) and organic carbon. The organic carbon was determined by an instrument, which incinerates the sample in an oxygen flow and an IR cell, subsequently analyses the CO$_2$ generated during the incineration.

The O$_2$, CO, and SO$_2$ concentrations in the kiln inlet, CO and O$_2$ out of the preheater, the flows of petcoke and tire ships and the temperatures in the calciners were recorded as process data corresponding to the days of the samples. Table 9-4 shows the concentration range of the O$_2$, CO and SO$_2$ measurements in the kiln inlet and preheater, and the production rate and the calciner temperatures during the period of sampling.

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9.3 Investigation of Sulfur Evaporation on the Process

Hot meal samples were taken from the bottom cyclone of strings A and B at 8 separate days during a month period. During this period, one sample from each calciner string was taken during normal operation, but on sampling days 5 and 6 only one sample was taken from B string because the A-string was out of operation. During the visit on sampling day 3 and 4, the following samples were taken:

- Sampling day 3: two samples during normal operation and three samples (two from string A and one from B) during a period where the RDF was increased in calciner A.
- Sampling day 4: two samples (one from string A and one from B) during a period with increased tire chips injection in the kiln inlet.

The samples were sent to the FLSmidth A/S laboratory for analyses of the chemical composition (by X-Ray diffraction) and organic carbon. The organic carbon was determined by an instrument, which incinerates the sample in an oxygen flow and an IR cell, subsequently analyses the CO$_2$ generated during the incineration.

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During the sampling period the cement plant operated with high concentration of oxygen, which varied from 4 to 10 vol. %, and subsequent low CO concentrations, below 0.02 vol. %, both in the kiln inlet and in the preheater.

Table 9-5 summarizes the hot meal analysis of the all samples taken for this investigation and it can be seen that the content of minor components, such MgO, MnO, TiO_2, P_2O_5, and SrO, have a small variation (less than 0.05 wt. % in standard deviation) in the 19 hot meal samples. However, SiO_2 and CaO, which are important components for the clinker, are having large standard deviations of 1.66 and 3.32 wt. %, respectively. The Al_2O_3 and Fe_2O_3 content, which are the other main oxides in the clinker, vary to less extent with a standard deviations of 0.5 and 0.25 wt. %, respectively. The Cl, K_2O and SO_2 contents present similar standard deviations as the main oxides, giving 0.62, 0.56 and 0.26 wt. %, respectively. The greatest variation is in the loss on ignition (LOI), which range from 1.87 to 17.9 wt. %. The loss on ignition indicates how incomplete the calcination was. The organic carbon from the hot meal samples during normal operation varies from 0.03 to 0.12 wt. % with an average of 0.06 wt. %. When RDF firing was increased the organic carbon varied from 0.03 to 0.07 wt. %, and when the firing of tires chips in the kiln inlet was increased the organic carbon varied from 0.05 to 0.1 wt. %.

The fixed installation of the cement plant recorded always a SO_2 concentration of 0 ppm in the kiln inlet during the sampling period, as shown in Table 9-4. Therefore, the organic carbon variation from the hot meal samples cannot be related to the SO_2 in the kiln inlet. However, it may be possible that the content of organic carbon measured in the hot meal under those conditions provokes a minor SO_2 release that the analyzer was unable to detect.

<table>
<thead>
<tr>
<th>O_2 [vol. %]</th>
<th>CO kiln inlet [vol. %]</th>
<th>SO_2 kiln inlet [ppm]</th>
<th>CO preheater [vol. %]</th>
<th>Production each string [t/day]</th>
<th>T calciner [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-9</td>
<td>≤ 0.02</td>
<td>0</td>
<td>4-10</td>
<td>0-0.2 spikes to 0.4</td>
<td>2000-2500</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>881-1013</td>
</tr>
</tbody>
</table>

Table 9-4: Concentration range of the gas measurements (O_2, CO and SO_2) in the kiln inlet and preheaters, the production range and the temperature of the calciner for normal operation. Target calciner temperature: 875 °C.

During the sampling period the cement plant operated with high concentration of oxygen, which varied from 4 to 10 vol. %, and subsequent low CO concentrations, below 0.02 vol. %, both in the kiln inlet and in the preheater.

Table 9-5 summarizes the hot meal analysis of the all samples taken for this investigation and it can be seen that the content of minor components, such MgO, MnO, TiO_2, P_2O_5, and SrO, have a small variation (less than 0.05 wt. % in standard deviation) in the 19 hot meal samples. However, SiO_2 and CaO, which are important components for the clinker, are having large standard deviations of 1.66 and 3.32 wt. %, respectively. The Al_2O_3 and Fe_2O_3 content, which are the other main oxides in the clinker, vary to less extent with a standard deviations of 0.5 and 0.25 wt. %, respectively. The Cl, K_2O and SO_2 contents present similar standard deviations as the main oxides, giving 0.62, 0.56 and 0.26 wt. %, respectively. The greatest variation is in the loss on ignition (LOI), which range from 1.87 to 17.9 wt. %. The loss on ignition indicates how incomplete the calcination was. The organic carbon from the hot meal samples during normal operation varies from 0.03 to 0.12 wt. % with an average of 0.06 wt. %. When RDF firing was increased the organic carbon varied from 0.03 to 0.07 wt. %, and when the firing of tires chips in the kiln inlet was increased the organic carbon varied from 0.05 to 0.1 wt. %.

The fixed installation of the cement plant recorded always a SO_2 concentration of 0 ppm in the kiln inlet during the sampling period, as shown in Table 9-4. Therefore, the organic carbon variation from the hot meal samples cannot be related to the SO_2 in the kiln inlet. However, it may be possible that the content of organic carbon measured in the hot meal under those conditions provokes a minor SO_2 release that the analyzer was unable to detect.

<table>
<thead>
<tr>
<th>O_2 [vol. %]</th>
<th>CO kiln inlet [vol. %]</th>
<th>SO_2 kiln inlet [ppm]</th>
<th>CO preheater [vol. %]</th>
<th>Production each string [t/day]</th>
<th>T calciner [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-9</td>
<td>≤ 0.02</td>
<td>0</td>
<td>4-10</td>
<td>0-0.2 spikes to 0.4</td>
<td>2000-2500</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>881-1013</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Test 1</th>
<th>Test 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal</td>
<td>Normal</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Inorganic Composition</th>
<th>Test 1</th>
<th>Test 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CaO</strong></td>
<td>62.44</td>
<td>63.31</td>
</tr>
<tr>
<td><strong>SrO</strong></td>
<td>0.15</td>
<td>0.14</td>
</tr>
<tr>
<td><strong>B</strong></td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td><strong>O</strong></td>
<td>0.03</td>
<td>0.03</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Process</strong></th>
<th><strong>Sampling day</strong></th>
<th><strong>Chemical</strong></th>
<th><strong>Chapter 9: Industrial Experience on Sulfur Release</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SrO</strong></td>
<td>day 8</td>
<td>0.15</td>
<td>0.14</td>
</tr>
<tr>
<td><strong>B</strong></td>
<td>day 8</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td><strong>O</strong></td>
<td>day 8</td>
<td>0.03</td>
<td>0.03</td>
</tr>
</tbody>
</table>
When RDF in calciner A was increased from 37 to 85 % RDF of fuel input (test 1), the organic carbon in the samples corresponded to the lower range of the organic carbon content during normal operation. According to this observation and the fuel analysis, the RDF contains 90 % of combustible material and it was well combusted in the calciner.

The organic carbon from the hot meal samples correlates to the percentage of fuel input to the each calciner coming from petcoke as shown in Figure 9-9, calculated according to equation 9.1.

Figure 9-9: Relationship between the percentage of petcoke as fuel input in the calciner and the organic carbon of hot meal samples.

The results show that the organic carbon increased when higher petcoke and lower RDF were fired. As such, it may be concluded that the organic carbon is the unconverted carbon coming from the petcoke, since it has higher content of fixed carbon than RDF. According to Figure 9-9, it would be advantageous to fire higher content of RDF. However, the cement plant have found by experience that the limitation for firing large amounts of RDF is the CO emissions in the stack, where the daily accumulated limit of CO, which is 350 mg/Nm$^3$ CO @ 10 vol. % O$_2$, cannot be exceeded.

9.3.1 Fuel Conversion in the Calciner

Table 9-6 summarizes the gas concentrations in the kiln inlet, the preheater, the fuel flows in the calciner, the production flow, the content of organic carbon in the hot meal, the degree of char conversion, and the total conversion in the calciner to the corresponding time when the hot meal sample was taken.

The CO concentration measured in the preheater gives an indication of the combustion in the calciner. The high content of O$_2$ and the low content of CO in the kiln inlet and in the preheater ensured a good combustion.

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<table>
<thead>
<tr>
<th>Day</th>
<th>Operation</th>
<th>Normal Sampling</th>
<th>Petcoke</th>
<th>CO</th>
<th>SO</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
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<tr>
<td>5</td>
<td></td>
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<tr>
<td>4</td>
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</tr>
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<td>3</td>
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</tr>
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</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 9-6: Summary of the process data in the kiln inlet, the preheater, the fuel flows in the calciner, the production flow, the organic conversion and the degree of char conversion at the total conversion in the calciner when the hot meal sample was taken. Note: Calculated using equation 9.1 from the RDF % fue carbon in the hot meal, the degree of char conversion and production flow.

Chapter 9: Industrial Experience on Sulfur Release
The degree of char conversion is calculated from the carbon introduced by the petcoke and the RDF and the organic carbon determined in the samples taken in the bottom stage cyclone. The degree of char conversion in the calciner varies from 93.7 to 99.5% with an average of 98.2%. Figure 9-10 shows the relationship between the percentage of petcoke as fuel input and the degree of char conversion in the calciner.

The total degree of conversion is based on the total conversion of combustible material, which comprises the volatiles and the fixed carbon of both RDF and petcoke fired. Figure 9-11 shows the total degree of conversion of the combustible material as function of the petcoke percentage of fuel input in the calciner. The total degree of fuel conversion in the calciner varies from 97.4 to 99.6% with an average of 99.1%, which also shows that the combustible material fuel is fully combusted in the calciner.

According to Figure 9-10 and Figure 9-11, if the degree of char conversion and the total degree of conversion are higher than 90% for the different percentage of petcoke fired, which means that the calciner fuel is fully converted in the calciner.

### 9.3.2 Tendency of Build-ups

The SO$_3$ and Cl contents in the hot meal samples were determined because these concentrations may predict the tendency of the build-ups formation in the kiln system according to Figure 9-12. The diagram, previously presented in Chapter 4, is based on industrial experience using fossil fuels and is divided in 3 zones: low, medium, and high build-up tendency. In the graph points corresponding to samples taken during a process instability, normal operation, test 1, test 2, and samples taken from string B while there was a build-up in string A are plotted.
It can be seen that the samples taken during normal operation are situated in the zone corresponding to medium tendency build-up. The point in the high build-up tendency region from test 2 originates from string A, which experienced a blockage 2 days after sampling, where string A was stopped corresponding to sampling day 5 and 6. The other point in the high build-up tendency region during the normal operation corresponds to string B during the sampling day 2, this string also experienced blockage the following day. The samples taken while the string experiences are very close to the limit of high build-up tendency region, which could indicate the cause of the observed build-ups. The build-ups, which this cement plant experiences, are normally present in the bottom stage cyclone and in the riser duct.

9.3.3 Sulfur Volatility

The volatility of the sulfur in the kiln can be described using an evaporation factor, as described in Chapter 4. The sulfur evaporation factor, $\varepsilon_s$, is defined according to equation 9.2.

$$\varepsilon_s = \frac{w_{SO_3, hotmeal, LOI free}}{w_{SO_3, clinker}}$$

[9.2]

where $w_{SO_3, hotmeal, LOI free}$ is the content of SO$_3$ in the hot meal on LOI free basis and $w_{SO_3, clinker}$ is the content of SO$_3$ in the clinker. The dust circulation from the coolers and the kiln to the bottom stage cyclone has been disregarded. The clinker produced was analyzed every second hour by the cement plant laboratory. It is assumed that the clinker analysis corresponds to the hot meal sample after 30 min from the time of sampling, which corresponds approx. to the residence time of the solid material in the rotary kiln. The SO$_3$ content in the
clinker is summarized in Table H-1 in Appendix H, which shows the clinker analysis of the corresponding hot meal samples.

Table 9-7 shows the range of the sulfur evaporation factor during the normal operation and for test 1 and 2.

<table>
<thead>
<tr>
<th></th>
<th>Normal operation</th>
<th>Test 1</th>
<th>Test 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur evaporation factor</td>
<td>0.25-0.54</td>
<td>0.38-0.46</td>
<td>0.42-0.46</td>
</tr>
</tbody>
</table>

It can be seen that the tests performed does not change the sulfur evaporation. Figure 9-13 shows the sulfur evaporation factor as function of the organic carbon of the hot meal samples. It can be seen that there is no clear relationship. This supports the experiments using wood with different degree of devolatilization, presented in Chapter 5, where char caused less much sulfur release than the volatiles.

9.4 Conclusions for the Industrial Experience and Challenges

Hot meal sampling and multicomponent gas measurements with focus on SO$_2$, CO and O$_2$ in the kiln inlet were performed in a cement plant with the aim of determining the relationship between organic carbon in the bottom stage cyclone and the SO$_2$ in the kiln inlet. Two tests were performed: 1) an increase of RDF firing in calciner A and 2) an increase of tire chips injection in the kiln inlet.
There were differences in the CO and SO$_2$ concentration measured with the hot FTIR gas measurement equipment and the cold gas measurement equipment. The cold gas measurement equipment was not able to detect spikes of SO$_2$ and CO occurring in brief periods when the two tests were performed.

During the sampling period, the organic carbon from the hot meal samples varied from 0.03 to 0.2 wt. % with an average of 0.06 wt. % and the gas analysis recorded by fixed equipment showed always 0 ppm SO$_2$ in the kiln inlet. Therefore, it was not possible to identify a relationship between organic carbon and SO$_2$ in the kiln inlet from these measurements. However, it cannot be excluded that the organic carbon in the hot meal is related to the SO$_2$ release in the kiln inlet.

A relationship between the organic carbon and the percentage of petcoke fired in the calciner was found. The organic carbon increased when more petcoke (and less RDF) was fired. The degree of char conversion in the calciner and the total degree of fuel were higher than 90%, which indicate that the calciner fuel was well combusted in the calciner.

Build-ups and process instabilities experienced by the cement plant correspond to SO$_3$ and Cl levels in the analyzed hot meal in or close to the region of high build-up tendency for fossil fuels. There is a good consistency between the predictions of build-ups by the diagram and the reality, this tool could therefore be potentially used to detect and avoid future build-ups when firing alternative fuels.

Nowadays there still exist challenges on the measurements to control process stability and predict instability situations. The SO$_2$ concentration in the kiln is fast continuous variable used to control the cement plant operation. However, the measurement of SO$_2$ in the kiln is difficult due to the high content of dust in the gas and the technology used is not always able to measure it because the dust absorbs the SO$_2$. Analysis of SO$_3$ and Cl in the hot meal is another indication for process instability but it is time consuming to take the sample, analyze it, and react on the process control. From an economical and practical point of view, it is more convenient for the cement plants to have a fast indication of the process stability by continuous gas measurements instead of the hot meal sampling.
10. Final Conclusions

An improved understanding of sulfur release during fuel combustion in the kiln inlet of cement rotary kilns has been gained through this Ph.D. project through review of the existing literature, pilot and full-scale experimental investigations, and mathematical modeling.

10.1 Main Results and Conclusions

The main conclusions to be drawn from the literature review are:

- Cement production is a very energy-consuming process. There is an interest in replacing fossil fuels with selected waste, biomass and industrial by-products with recoverable calorific value, defined as alternative fuels, in order to minimize production cost, i.e. due to increasing fossil fuel prices and environmental concerns.

- The combustion of alternative fuels is more challenging than combustion of fossil fuels, due to the lack of experience in handling the different and varying combustion characteristics caused by different chemical and physical properties, e.g. higher moisture content and larger particle sizes. New combustion equipments or modifications of existing plant layouts have been developed but alternative fuels are often directly fired in the calciner and/or to the main burner despite the large particle sizes because this requires a minimum of investments.

- Sulfur, chloride, sodium, and potassium, which are volatile elements, evaporate when exposed to high temperature in the burning zone and subsequently condense in colder parts of the plant. High concentrations of volatile elements often cause difficulties in kiln operation and plant stability by causing build-ups, kiln rings and/or shell corrosion.

- When unconverted or partly converted alternative fuels drop into the rotary kiln inlet and are combusted in direct contact with the bed material, local reducing conditions may occur. The volatiles released from the fuels may therefore react with sulfates present in the hot meal and form gaseous SO$_2$.

- Previous studies of sulfur release during combustion of alternative fuel particles have shown that reducing gases from the fuel devolatilization cause reductive decomposition of CaSO$_4$ and indicated that the fuel particle size is of high importance for the degree of sulfur release.

- Investigations of the reductive decomposition of CaSO$_4$ showed that CaO, CaS, or mixtures of both products are favored depending on the temperature and the type and concentration of the reducing gas. The most influencing parameter to the reaction rate of reduction of CaSO$_4$ is the partial pressure of the gaseous reductive agent.

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Chapter 10: Final Conclusions

The main results and conclusions regarding sulfur release in the material inlet of cement rotary kiln are:

- The inorganic chemistry was studied by thermodynamic calculations in order to improve understanding of the chemistry. The reducing agents in the gas phase decreased the stability of CaSO₄ and increased the stability of SO₂ in the kiln inlet at temperatures between 900 and 1100 °C. The volatility of the chlorine was not affected by the gas atmosphere, but was very sensitive to the temperature. Higher levels of alkali compared sulfur reduced the sulfur release to the gas phase, but increased the amount of compounds in liquid phase in the kiln and the alkali species in the gas phase.

- The pilot plant experiments in the high temperature rotary drum using pine wood and tire rubber particles were performed in order to investigate the effect of particle size, fuel conversion degree, sulfur load in the bed and moisture content of the fuel on the release of sulfur. The effect of fuel particle size on sulfur release showed that smaller particles increase the SO₂ release because they were heated faster and thus released the volatile gases faster and with higher concentrations because stronger local reducing conditions were formed. The effect of wood cylinders with different degree of volatiles showed that the sulfur release mainly took place during devolatilization, corresponding to the cases of virgin wood and wood char made at 300 and 500 °C. This was supported by the findings of the industrial investigation on sulfur released, where no clear relationship was observed between the organic carbon (char) from the fuel entering in the rotary kiln and the sulfur evaporation factor.

- The effect of different concentrations of CO, H₂, and CH₄ on sulfur release was investigated experimentally at different temperatures, oxygen contents and times of exposure. The experiments using a single reducing agent indicated a threshold concentration below which SO₂ release does not occur. The effect of the different concentrations can be related to the effect of gases released from alternative fuels. The concentration of the reducing agent and the time of exposure were of high importance for SO₂ release because it was found that a high concentration of the reducing agent in a short period (representing devolatilization) led to a higher total SO₂ amount compared to the a low concentration during a long period (representing char combustion or devolatilization of large fuel particles).

- The experimental results of binary mixtures when CO was present showed that SO₂ increases with increasing CO concentration in the mixture. Similar SO₂ release was obtained for the different mixtures of CH₄ and H₂.

- A mathematical model, which was able to predict sulfur release caused by volatiles from wood particles fired in the material kiln inlet was developed based on the reaction between the volatiles and CaSO₄ in the bed material in CSTR in series. The effect of the fuel degree of coverage, the bed fill degree, and the bed sulfur content and firing degree on sulfur release was investigated. The sulfur evaporation factor increased with decreasing particle mass, sulfur content in the bed and fill degree,
while it decreased with increasing the fuel degree of coverage. The firing degree and the fuel degree of coverage were identified by the sensitivity analysis as the most influencing factors for the total SO₂ release and the sulfur evaporation factor, while the kinetic parameters did not modify the output results. The model evaluation showed that the model follows the experimental data tendency.

- A model to predict the tendency of build-ups of a kiln system based on the SO₂ and Cl concentrations in the hot meal was developed. For a cement plant with 3500 tons per day without bypass using raw materials with 0.05 wt. % S and 0.01 wt. % Cl and fuel with 5 wt. % S and 0.001 wt. % Cl, the tendency of build-ups predicted was in the medium/high line, while using bypass the tendency of build-ups was medium, close to the low region. The model also predicted medium tendency build-ups when alternative fuels are fired in the kiln inlet. A sensitivity analysis was performed in order to investigate the effect of the parameters on the SO₂ and Cl content of the hot meal and showed that the chlorine evaporation factor has the largest influence with almost 400 % deviation on the Cl concentration.

### 10.2 Recommendations

When considering alternative fuel utilization in the calciner or in the riser duct, the particle size and fuel flow are key parameters to ensure a proper combustion before the particles reach the bed material in the kiln inlet causing sulfur release. Shredding large fuel particles would be the first recommendation to avoid their combustion in contact with the bed material and thereby avoid sulfur release in the kiln inlet. However, if the combustion of small particles in large amounts is not complete, high sulfur release may take place due to the particle size and elevated number of particles. The sulfur release may decrease when operating the kiln with an oxygen concentration above 5 vol. % in the kiln inlet, which is also recommended if the fuel is not downsized. Since no SO₂ release takes place below a threshold concentration of reducing agent/s, a threshold fuel flow for the kiln inlet may exist, giving no sulfur release because the concentration of the reducing agents released are below the threshold. However, each kiln may have its own threshold fuel flow in the kiln inlet, which would depend on the kiln characteristics and raw materials and fuels used. Thereby a general recommendation in this aspect is difficult to make.

Gas stratification in the rotary kiln has been reported by measurements (Hansen, 2002) and predicted by CFD modeling. Figure 10-1 and Figure 10-2, which are cordially provided by Aixergee Process Optimization, show the O₂ and CO₂ gas concentrations, respectively, in the inlet of the rotary kiln for an ILC-kiln system with 2 string. It can be seen that both concentrations are stratified, meaning that the concentration is increasing/decreasing in layers and is not uniform in the entire freeboard. The model allows the mixing inflow, however, the results show that there is a poor mixing between the gas and the bed material (no gas penetration into the bed material) and the bed material is contact with the lowest concentration of O₂ and the highest of CO₂.

Chapter 10: Final Conclusions

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This effect may influence the combustion of alternative fuel particles in the kiln inlet and subsequently the sulfur release. In order to prevent or minimize gas stratification, mixing devices can be applied in the kiln inlet to enhance turbulence flow and optimize the fuel combustion. These mixing devices may minimize the sulfur release, because of the uniformity of the gas atmosphere and the time of contact between the fuel and material may be reduced. However, they may have a short service life due to abrasion, thermal stress or mechanical stress. Other ways of breaking the gas stratification may also have a positive effect reducing sulfur release.

The sulfur release in the inlet of the rotary kiln can be avoided when the volatile gases from fuels are not released in contact with the bed material, thereby, only allowing fuel char to be in contact with the kiln bed material. Assuming a cement plant with a production of 3500 tons per day that operates the rotary kiln with 5 vol. % O₂, the maximum char fuel flow introduced into the rotary kiln can be calculated based on the minimum gas flow for the char combustion and the actual gas flow in the kiln inlet, which is 0.5 kg gas/kg clinker. The fuel char is assumed to consist of carbon. For the pine wood with 44.7 wt. % C, the maximum wood char flow is 3377 kg/h. However, this amount of char would consume all the oxygen content in the gas phase, which is undesirable for the process. It would be reasonable to assume that between 1/4 and 1/10 of the maximum char flow could be introduced into the rotary kiln without causing undesired effects, because the oxygen content should not decrease drastically. Thereby, the real char flow into the rotary kiln is between 845 to 340 kg/h wood char, which would correspond to 7300-3000 kg wood/th for a wood with 11.3 wt. % fixed carbon.

Considering tire rubber with 87 wt. % C, the maximum char fuel is 1700 kg/h and the real char flow varies between 430 to 170 kg/h tire char, corresponding to 1300-520 kg/h tire (for a tire rubber with 32.6 wt. % fixed carbon). The tire rubber flow fired in the riser duct in the industrial campaign, where 4000-5000 tons of clinker was produced, are around the same order of magnitude as the calculated results.
Sulfur release from the kiln bed material can also be minimized when fuel combustion takes place at temperatures below 800 °C. This may imply to have a different configuration of the kiln system with the place of fuel combustion, in which the fuel combustion is completed at lower temperatures and the hot flue gas is used for calcination.

10.3 Suggestions for Future Work

The model to predict sulfur release in the kiln inlet due to alternative fuels firing has been successfully developed and evaluated against experimental data. However, the model could be optimized with respect to predicting the SO\textsubscript{2} release when the sulfur concentration in the kiln bed material is varied, which is related to the particle motion in the bed and rotational speed. The particle motion could be relevant to include but also difficult, and CFD tools may be needed.

A comparison between the model and the pilot-scale data implies that the model over-estimates the SO\textsubscript{2} concentration compared to the experiment results at 10 vol. % O\textsubscript{2}. Hence, the effect of the oxygen in the freeboard atmosphere should be further implemented. Furthermore, the kiln model and tendency of build-ups model should be validated against full-scale data and thereby, the absorption of SO\textsubscript{2} on the dust carried by the kiln gas could be also included.

The effect of the gas stratification in the high temperature rotary kiln may be difficult to achieve but the effect of the gas atmosphere, i.e. different CO\textsubscript{2} concentrations together with O\textsubscript{2}, could be further experimentally investigated.

Experiments with mixing devices in the rotary kiln could be investigated in order to optimize the fuel combustion in direct contact with the kiln bed material, and characterize the effect on sulfur release.

10.4 References

## List of Symbols

### Abbreviations and acronyms

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>a.r.</td>
<td>As received</td>
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Appendix A: Equilibrium Calculations

- Equilibrium between SO₂ and SO₃

The equilibrium concentration as function of the temperature for reaction (A-1) is shown in Figure A-1.

\[ \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{SO}_3(g) \]  \hspace{1cm} (A-1)

This phenomenon can also be seen by the free Gibbs Energy of the equilibrium reaction (A-1), which is mathematically expressed by equation A.1.

\[ \Delta G = \Delta G^\circ + R \cdot T \cdot \ln \left( \frac{P_{\text{SO}_3}}{P_{\text{SO}_2} \cdot P_{\frac{1}{2}\text{O}_2}} \right) \]  \hspace{1cm} [A.1]

where \( \Delta G^\circ \) is the free Gibbs energy at standard conditions (298.15 K and 1 atm), which is -141.8 kJ, R is the universal gas constant (8.314 J/mol·K), T is the absolute temperature in K and \( P_i \) is the partial pressure of the component i.

- Gibbs Energy Minimization

The equilibrium of a closed thermodynamic system is established when its Gibbs energy at constant temperature and pressure has reached its minimum.
Appendices

Gibbs Energy of the system of one or more phases is given by equation A.3.

\[ G = \sum \sum n_i^k \cdot \mu_i^k \]  

where \( k \) is the number of different phase, \( n_i \) is the molar amount of the phase constituent \( i \), \( \mu_i \) is the chemical potential of a phase constituent \( i \).

At equilibrium the chemical potential of each element or compound at each phase is equal (equation A.5). The chemical potential is defined by equation A.4.

\[ \mu_i^e = \mu_i^r = \mu_i^r \]

\[ \mu_i = \mu_i^0 + RT \cdot \ln a_i = \mu_i^0 + RT \cdot \ln x_i y_i \]

where \( a_i \) is the activity and \( y \) is the activity coefficient. Thereby, equation A.3 can be rewritten as:

\[ G = \sum \sum n_i^k (\mu_i^0 + RT \cdot \ln x_i y_i) \]

The minimum value of Gibbs energy is found also when masses of the system components remain constant (mass balance constraints). This is mathematically expressed by A.7.

\[ b_j = \sum \sum n_i^e \cdot a_i \]

where \( b \) is the molar amount of the system component \( j \), \( n \) is the molar amount of the constituent \( i \) in phase \( \alpha \) and \( a_i \) is the stoichiometric coefficient of the system component \( j \) in constituent \( i \).

FactStage uses ChemApp library during the process to minimize Gibbs energy.
Appendix B: Species included in the Thermodynamic Calculations

For the equilibrium calculations of Chapter 4, ideal gas phase compounds, pure solid phases, and pure liquid phases were included from the FactSage 6.2 compound database. The species included in the full calculations (section 4.4.1) from the compound database are listed below. For the simplified model (section 4.4.2) these species are also considered, excluding the species marked in bold.

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| SiO2 | SiO2 | (Na2O)2 | (Na2O)2 | (Na2O)2 | (Na2O)2 | (Na2O)2 | (Na2O)2 |
| Al2O3 | Al2O3 | Al2O3 | Al2O3 | Al2O3 | Al2O3 | Al2O3 | Al2O3 |
| Si | Si | Si | Si | Si | Si | Si | Si |
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| Na2S | Na2S | Na2S | Na2S | Na2S | Na2S | Na2S | Na2S |
| AlS3 | AlS3 | AlS3 | AlS3 | AlS3 | AlS3 | AlS3 | AlS3 |
| SiC | SiC | SiC | SiC | SiC | SiC | SiC | SiC |
| K2SO4 | K2SO4 | K2SO4 | K2SO4 | K2SO4 | K2SO4 | K2SO4 | K2SO4 |
| Ca | Ca | Ca | Ca | Ca | Ca | Ca | Ca |
| Fe | Fe | Fe | Fe | Fe | Fe | Fe | Fe |

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### Pure liquids phases

| Na2O | Al2O3 | SiO2 | K2O | CaO | NaO | Na | Ca2O |
| NaCN | NaCN | NaCN | NaCN | NaCN | NaCN | NaCN | NaCN |
| SiO2 | SiO2 | (Na2O)2 | (Na2O)2 | (Na2O)2 | (Na2O)2 | (Na2O)2 | (Na2O)2 |
| Al2O3 | Al2O3 | Al2O3 | Al2O3 | Al2O3 | Al2O3 | Al2O3 | Al2O3 |
| Si | Si | Si | Si | Si | Si | Si | Si |
| SO2 | SO2 | SO2 | SO2 | SO2 | SO2 | SO2 | SO2 |
| Na2S | Na2S | Na2S | Na2S | Na2S | Na2S | Na2S | Na2S |
| AlS3 | AlS3 | AlS3 | AlS3 | AlS3 | AlS3 | AlS3 | AlS3 |
| SiC | SiC | SiC | SiC | SiC | SiC | SiC | SiC |
| K2SO4 | K2SO4 | K2SO4 | K2SO4 | K2SO4 | K2SO4 | K2SO4 | K2SO4 |
| Ca | Ca | Ca | Ca | Ca | Ca | Ca | Ca |
| Fe | Fe | Fe | Fe | Fe | Fe | Fe | Fe |
**Pure solid phases**

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**Pure solid phases**

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Appendix C: Data from the Experiments using Reducing Agents

- Example of obtained Data

Original data obtained in the experiments presented in Chapter 6 is exemplified in Figure C-1, which shows the constant SO\textsubscript{2} concentration for different CO concentrations introduced in different experiments. The duration of the period where CO was introduced under the bed material for each concentration was 4 or 5 min in order to reach a steady-state and have a constant SO\textsubscript{2} concentration. The results shown in Chapter 6 are the averages of the constant SO\textsubscript{2} concentrations and the standard deviations of results.

![Figure C-1](image)

**Carbon Balance**

The carbon mass balance was checked by considering the molar mass flow rate of CO introduced and CO\textsubscript{2} measured by the gas analyzer, according to equation C.1. The deviation of the results is calculated according to equation C.2.

\[
\delta_{CO} = \frac{\dot{N}_{CO} - \dot{N}_{CO_{2}}}{\dot{N}_{CO}} \times 100 \tag{C.1}
\]

\[
Deviation(\%) = \frac{\dot{N}_{CO} - \dot{N}_{CO_{2}}}{\dot{N}_{CO}} \times 100 \tag{C.2}
\]

The CO\textsubscript{2} concentration measured by the analyzer needed to be corrected for the mass balance because the CO\textsubscript{2} coming from the air of the freeboard atmosphere need to be subtracted. The base lines are 215-248 ppm CO\textsubscript{2} when using 5 vol. % O\textsubscript{2} and 383 ppm CO\textsubscript{2} when using 10 vol. % O\textsubscript{2}. The data for the experiments performed
at 900 °C at 5 and 10 vol. % O<sub>2</sub> are shown in Table C-1 and C-2, respectively, and Table C-3 shows the data for the experiments performed at 1000 °C.

### Table C-1: Carbon balance and deviation for the experiments performed at 900 °C and 5 vol. % O<sub>2</sub>. Note: Base line for CO<sub>2</sub> from the air content of the freeboard atmosphere is 215 ppm.

<table>
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<tr>
<th>Flow [NL/min]</th>
<th>CO conc. [vol. %]</th>
<th>kmol CO/min = kmol C/min</th>
<th>kmol CO without base line [ppm]</th>
<th>Deviation [%]</th>
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<tr>
<td>5</td>
<td>0.05</td>
<td>2.23 · 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>101</td>
<td>2.11 · 10&lt;sup&gt;-4&lt;/sup&gt;</td>
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<tr>
<td>7</td>
<td>0.07</td>
<td>3.12 · 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>101</td>
<td>2.87 · 10&lt;sup&gt;-4&lt;/sup&gt;</td>
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<tr>
<td>10</td>
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<td>4.46 · 10&lt;sup&gt;-4&lt;/sup&gt;</td>
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<td>4.26 · 10&lt;sup&gt;-4&lt;/sup&gt;</td>
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<tr>
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<td>6.69 · 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>101</td>
<td>6.20 · 10&lt;sup&gt;-4&lt;/sup&gt;</td>
</tr>
<tr>
<td>20</td>
<td>0.2</td>
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### Table C-2: Carbon balance and deviation for the experiments performed at 900 °C and 10 vol. % O<sub>2</sub>. Note: Base line for CO<sub>2</sub> from the air content of the freeboard atmosphere is 383 ppm.

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<th>Flow [NL/min]</th>
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<th>kmol CO/min = kmol C/min</th>
<th>kmol CO without base line [ppm]</th>
<th>Deviation [%]</th>
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<td>10</td>
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</tbody>
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### Table C-3: Carbon balance and deviation for the experiments performed at 900 °C and 10 vol. % O<sub>2</sub>. Note: Base line for CO<sub>2</sub> from the air content of the freeboard atmosphere is 248 ppm.

<table>
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<tr>
<th>Flow [NL/min]</th>
<th>CO conc. [vol. %]</th>
<th>kmol CO/min = kmol C/min</th>
<th>kmol CO without base line [ppm]</th>
<th>Deviation [%]</th>
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at 900 °C at 5 and 10 vol. % O<sub>2</sub> are shown in Table C-1 and C-2, respectively, and Table C-3 shows the data for the experiments performed at 1000 °C.

### Table C-4: Carbon balance and deviation for the experiments performed at 1000 °C and 5 vol. % O<sub>2</sub>.

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<th>CO conc. [vol. %]</th>
<th>kmol CO/min = kmol C/min</th>
<th>kmol CO without base line [ppm]</th>
<th>Deviation [%]</th>
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</thead>
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<tr>
<td>5</td>
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<td>2.11 · 10&lt;sup&gt;-4&lt;/sup&gt;</td>
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<tr>
<td>7</td>
<td>0.07</td>
<td>3.12 · 10&lt;sup&gt;-4&lt;/sup&gt;</td>
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<tr>
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<td>0.1</td>
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<td>101</td>
<td>8.50 · 10&lt;sup&gt;-4&lt;/sup&gt;</td>
</tr>
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</table>
The corresponding CO$_2$ concentrations measured for each experiment of section 6.3 are plotted as the average of the constant concentrations and the standard deviations of results. Figure C-2 shows the CO$_2$ concentrations for different CO concentrations used varying the oxygen concentration.

**Figure C-1:** CO$_2$ concentration when different CO concentrations were introduced under the bed material with 5 and 10 vol. % O$_2$. Experimental conditions: flow tube 1NL/min, 900 °C, 5 % fill degree, 2 wt. % CaSO$_4$, 100 NL/min, 6 rpm.

The CO$_2$ concentrations for different CO concentrations used varying the temperature are shown in Figure C-3.

**Figure C-2:** CO$_2$ concentration when different CO concentrations were introduced under the bed material at 900 and 1000 °C. Experimental conditions: flow tube 1 NL/min, 5 % fill degree, 2 wt. % CaSO$_4$, 100 NL/min with 5 vol. % O$_2$, 6 rpm.

**Figure C-3:** CO$_2$ concentration when different CO concentrations were introduced under the bed material at 900 and 1000 °C. Experimental conditions: flow tube 1 NL/min, 5 % fill degree, 2 wt. % CaSO$_4$, 100 NL/min with 5 vol. % O$_2$, 6 rpm.
The CO\textsubscript{2} concentrations corresponding to the experiments investigating the time of exposure of different CO concentrations at 900 and 1000 °C are plotted in Figure C-4 and Figure C-5, respectively.

Figure C-3: CO\textsubscript{2} concentrations when a total of 0.4 L of CO was introduced under the bed material with 5, 7, 10, 15, and 20 vol. % CO at 900 °C. Experimental conditions: flow tube 1 NL/min, 5 % fill degree, 2 wt. % CaSO\textsubscript{4}, 100 NL/min with 5 vol. % O\textsubscript{2}, 6 rpm.

Figure C-4: CO\textsubscript{2} concentrations when a total of 0.4 L of CO was introduced under the bed material with 5, 10, 15, and 20 vol. % at 1000 °C. Experimental conditions: flow tube 1 NL/min, 5 % fill degree, 2 wt. % CaSO\textsubscript{4}, 100 NL/min with 5 vol. % O\textsubscript{2}, 6 rpm.

For the different CH\textsubscript{4} concentrations experiments, the corresponding CO\textsubscript{2} concentrations varying the oxygen concentration are illustrated in Figure C-6.

Figure C-6: CO\textsubscript{2} concentration when different CH\textsubscript{4} concentrations were introduced under the bed material with 5 and 10 vol. % O\textsubscript{2}. Experimental conditions: flow tube 1NL/min, 900 °C, 5 % fill degree, 2 wt. % CaSO\textsubscript{4}, 100 NL/min, 6 rpm.

For the different CH\textsubscript{4} concentrations experiments, the corresponding CO\textsubscript{2} concentrations varying the oxygen concentration are illustrated in Figure C-6.
The corresponding CO$_2$ concentrations for different CH$_4$ concentrations used varying the temperature are illustrated in Figure C-7.

Figure C-5: CO$_2$ concentration when different CH$_4$ concentrations were introduced under the bed material at 900 and 1000 °C. Experimental conditions: flow tube 1 NL/min, 5 % fill degree, 2 wt. % CaSO$_4$, 100 NL/min with 5 vol. % O$_2$, 6 rpm.

The CO$_2$ concentrations corresponding to the experiments investigating the time of exposure of different CH$_4$ concentrations at 900 and 1000 °C are plotted in Figure C-8 and Figure C-9, respectively.

Figure C-6: CO$_2$ concentrations when a total of 0.4 L of CH$_4$ was introduced under the bed material with 5, 10, 15 and 20 vol. % CH$_4$ at 900 °C. Experimental conditions: flow tube 1 NL/min, 5 % fill degree, 2 wt. % CaSO$_4$, 100 NL/min with 5 vol. % O$_2$, 6 rpm.

Figure C-7: CO$_2$ concentrations when a total of 0.4 L CH$_4$ was introduced under the bed material with 5, 10, 15 and 20 vol. % CH$_4$ at 1000 °C. Experimental conditions: flow tube 1 NL/min, 5 % fill degree, 2 wt. % CaSO$_4$, 100 NL/min with 5 vol. % O$_2$, 6 rpm.

The CO$_2$ concentrations corresponding to the experiments investigating the time of exposure of different CH$_4$ concentrations at 900 and 1000 °C are plotted in Figure C-8 and Figure C-9, respectively.
The corresponding CO\textsubscript{2} concentrations for experiments of the mixtures of CO/CH\textsubscript{4} and CO/H\textsubscript{2} as function of the CO concentration are shown in Figure C-10, and for the experiments of the CH\textsubscript{4}/CO and CH\textsubscript{4}/H\textsubscript{2} mixtures as function of the CH\textsubscript{4} concentration in Figure C-11.

Figure C-8: CO\textsubscript{2} concentrations when mixtures CO/CH\textsubscript{4} and CO/H\textsubscript{2} were introduced under the bed material at 900 °C. Experimental conditions: flow tube 1 NL/min, 5 % fill degree, 2 wt. % CaSO\textsubscript{4}, 100 NL/min with 5 vol. % O\textsubscript{2}, 6 rpm.

Figure C-9: CO\textsubscript{2} concentrations when mixtures of CH\textsubscript{4}/CO and CH\textsubscript{4}/H\textsubscript{2} were introduced under the bed material at 900 °C. Experimental conditions: flow tube 1 NL/min, 5 % fill degree, 2 wt. % CaSO\textsubscript{4}, 100 NL/min with 5 vol. % O\textsubscript{2}, 6 rpm.
Appendix D: Kinetic Studies of CaSO₄ Reductive Decomposition

Kinetic studies of the reductive decomposition of CaSO₄ with CO and H₂ have been performed at different concentrations and temperature ranges by many authors (Diaz-Bossio et al., 1985; Xiao and Song, 2011; Zheng et al., 2011; Kim and Sohn, 2002; Talukdar et al., 1996). The activation energy and the pre-exponential factor found for the reductive decomposition of CaSO₄ with CO and H₂ according to reactions (D-1) and (D-2) are summarized in Table D-1. No kinetic parameters for the reductive decomposition of CaSO₄ with CH₄ have been reported.

\[ \text{CaSO}_4(s) + CO(g) \rightarrow \text{CaO}(s) + \text{SO}_2(g) + CO_2(g) \]  
(D-1)

\[ \text{CaSO}_4(s) + H_2(g) \rightarrow \text{CaO}(s) + \text{S}_2(g) + H_2O(g) \]  
(D-2)

The kinetic parameters for the reductive decomposition of CaSO₄ by CO found by Xiao and Song (Xiao and Song, 2011) are the ones used for the model because no CO₂ was introduced and the temperature range is relevant.

Appendix D References


Table D-1: Summary of the reported kinetic parameters for reductive decomposition of CaSO₄ by CO and H₂:

<table>
<thead>
<tr>
<th></th>
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<th></th>
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<th></th>
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<tr>
<td>(D-1) CO</td>
<td>variation 1–6 vol. % CO with 24 vol. % CO₂</td>
<td>900-1180</td>
<td>242 ± 33</td>
<td>7.4 ·10⁵</td>
<td>TGA</td>
<td>(Diaz-Bossio et al., 1985)</td>
<td></td>
</tr>
<tr>
<td>(D-1) CO</td>
<td>variation 0.1–1 vol. % CO</td>
<td>750–950</td>
<td>251.7</td>
<td>6.964 ·10⁶</td>
<td>Circulating fluidized bed reactor</td>
<td>(Talukdar et al., 1996)</td>
<td></td>
</tr>
<tr>
<td>(D-1) CO</td>
<td>20, 40 and 70 vol. % CO in N₂</td>
<td>880–950</td>
<td>145.3</td>
<td>1.89 ·10⁴</td>
<td>Isothermal bed reactor</td>
<td>(Xiao and Song, 2011)</td>
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<tr>
<td>(D-2) H₂</td>
<td>variation 1–6 vol. % H₂ with 24 vol. % CO₂</td>
<td>900–1180</td>
<td>288 ± 44</td>
<td>6.1 ·10⁶</td>
<td>TGA</td>
<td>(Diaz-Bossio et al., 1985)</td>
<td></td>
</tr>
</tbody>
</table>

The kinetic parameters for the reductive decomposition of CaSO₄ by CO found by Xiao and Song (Xiao and Song, 2011) are the ones used for the model because no CO₂ was introduced and the temperature range is relevant.

Appendix D References


Table D-1: Summary of the reported kinetic parameters for reductive decomposition of CaSO₄ by CO and H₂:

<table>
<thead>
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<tbody>
<tr>
<td>(D-1) CO</td>
<td>variation 1–6 vol. % CO with 24 vol. % CO₂</td>
<td>900-1180</td>
<td>242 ± 33</td>
<td>7.4 ·10⁵</td>
<td>TGA</td>
<td>(Diaz-Bossio et al., 1985)</td>
<td></td>
</tr>
<tr>
<td>(D-1) CO</td>
<td>variation 0.1–1 vol. % CO</td>
<td>750–950</td>
<td>251.7</td>
<td>6.964 ·10⁶</td>
<td>Circulating fluidized bed reactor</td>
<td>(Talukdar et al., 1996)</td>
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<tr>
<td>(D-1) CO</td>
<td>20, 40 and 70 vol. % CO in N₂</td>
<td>880–950</td>
<td>145.3</td>
<td>1.89 ·10⁴</td>
<td>Isothermal bed reactor</td>
<td>(Xiao and Song, 2011)</td>
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</tr>
<tr>
<td>(D-2) H₂</td>
<td>variation 1–6 vol. % H₂ with 24 vol. % CO₂</td>
<td>900–1180</td>
<td>288 ± 44</td>
<td>6.1 ·10⁶</td>
<td>TGA</td>
<td>(Diaz-Bossio et al., 1985)</td>
<td></td>
</tr>
</tbody>
</table>

The kinetic parameters for the reductive decomposition of CaSO₄ by CO found by Xiao and Song (Xiao and Song, 2011) are the ones used for the model because no CO₂ was introduced and the temperature range is relevant.

Appendix D References


Appendix E: CaSO₄ Particle Analysis

The particle size of CaSO₄ has been characterized by a Malvern with a repetition of 5 samples. The statistical results are listed below.

**Results Statistics:**

- **Distribution type:** Volume
- **Concentration:** 0.0066 vol. %
- **Density:** 1.000 g/cm³
- **Specific S.A.:** 3.2264 m²/g

**Mean diameters:**
- D (v, 0.1)= 0.97 μm
- D (v, 0.5)= 6.49 μm
- D (v, 0.9)= 28.74 μm

The cumulative particle distribution is shown in Figure E-1 and the raw data obtained is presented in Table E-1.

![Figure E-1: Cumulative particle distribution of the used CaSO₄.](image)
### Table E-2: Low and high particle size interval corresponding to the cumulative fraction for the CaSO₄ particle distribution.

<table>
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<td>258.95</td>
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Appendix F: Mass balance in basis of loss of ignition free

The solid mass flows of the raw meal and hot meal are calculated in loss of ignition free based according to equation F.1. The basis of loss of ignition free allows their comparison at different locations, after and before calcination.

\[
m_{j, \text{LOI free}} = \frac{m_j \cdot (100 - \text{LOI})}{100}
\]

where \(j\) = raw meal or hot meal

In Figure F-1, the typical material feed and hot meal (in black) and dust loss (in red) are specified. The net flows are calculated in order to check that at the different locations of the plant there is approximately 1 kg of material LOI free per kg of clinker. The dust from the rotary kiln is assumed to have 0 % LOI in order to calculate the net flow of the hot meal, and 15 % of the kiln dust is removed by the bypass.

<table>
<thead>
<tr>
<th>Component</th>
<th>Flow (kg/kg clinker)</th>
<th>LOI (% of clinker)</th>
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</thead>
<tbody>
<tr>
<td>Raw meal</td>
<td>1.75</td>
<td></td>
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<tr>
<td>Dust loss</td>
<td>0.142</td>
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<td>Net flow</td>
<td>1.602</td>
<td>36.1%</td>
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</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>Flow (kg/kg clinker)</th>
<th>LOI (% of clinker)</th>
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</thead>
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<tr>
<td>Hot meal</td>
<td>1.023</td>
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<tr>
<td>Dust loss</td>
<td>0.183</td>
<td>0 %</td>
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<tr>
<td>Net flow</td>
<td>1.21</td>
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</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>Flow (kg/kg clinker)</th>
<th>LOI (% of clinker)</th>
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</thead>
<tbody>
<tr>
<td>Rotary kiln</td>
<td>0.027</td>
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</tr>
<tr>
<td>Preheater tower + Calciner</td>
<td>1.023</td>
<td>36.1%</td>
</tr>
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</table>

Figure F-1: Solid mass flows material feed and hot meal (in black) and dust loss (in red) in basis of loss of ignition free in order to check that there is no formation or loss of material.
Appendix G: Industrial gas measurement system principles

- **Cold gas measurement system principle**

The fixed gas measurement system is located in kiln inlet. The gas measurement system can be divided in three main blocks as illustrated in Figure G-1.

![Figure G-1: Measuring principle of the process gas analysis system.](image)

The gas measurement system consists of:
- An extraction probe. The design of the extraction probe is identical for the cold gas measurement system and the hot FTIR measurement system. It consists of a tube with a steel cooling jacket with circulating water to keep the probe cool, so it can resist the high temperature in cement plants. The inner tube is heated to 200-210°C.

![Figure G-2: Schematic drawing of the applied extraction probe (FSLmidth A/S 2012a).](image)

- Sampling conditioning system. It consists of a gas cooler, a gas pump, a condensation pump, a flow meter and a filter with humidity sensor. The sample gas pump sucks the gas which is cooled to 5°C in the gas cooler to remove condensate water (FSLmidth A/S, 2012b).

- Analyzer. This cement plant has an infrared system to analyze SO2, CO, and NO, and paramagnetic for O2.

- Water cooled cooling jacket (50°C)

- Electrical heated sample probe (200°C)
The FTIR measurement system consists of the blocks shown in Figure G-1. The sampling conditioning system differs between the two techniques. In the FTIR measurement system the gas is not cooled. The heated pump contains a zirconium cell for analyzing the oxygen. The analyzer consists of an FTIR spectrometer, where the rest of the gas components, are analysed.

FTIR analyzes the gas composition by measuring the absorbance at different frequencies. The structure of the FTIR spectrometer is shown in Figure G-3. The spectrometer measures all the IR wavelengths simultaneously. FTIR has the advantage of being able to measure continuously and multicomponents simultaneously, such as NO, SO₂, CO₂, CO, H₂O, NH₃, HCl, and hydrocarbons from single measurement and interferences are automatically resolved. NH₃, HCl and hydrocarbons can be measured by the FTIR because the gas has not been cooled and these components have not condensed.

FTIR Spectrometer

Figure G-3: Scheme of the structure of FTIR spectrometer (Gasmet, 2013).

Appendix G References


Appendix H: Clinker composition for the industrial investigation

In order to calculate the sulfur evaporation factor, $SO_3$ content in the clinker is needed. The clinker analysis, which corresponds to the hot meal sample after 30 min from the time of sampling is summarized in Table H-1.

<table>
<thead>
<tr>
<th>Clinker composition (wt. % clinker based)</th>
<th>Free CaO</th>
<th>Alite</th>
<th>Aluminate</th>
<th>Ferrite</th>
<th>SO$_3$</th>
<th>Na$_{eq}$</th>
<th>Fluoride</th>
<th>Cl</th>
<th>P$_2$O$_5$</th>
<th>MgO</th>
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<td>Sampling day 1</td>
<td>0.8</td>
<td>65.8</td>
<td>7.5</td>
<td>12.3</td>
<td>1.3</td>
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<td>0.1</td>
<td>0</td>
<td>0.4</td>
<td>0.9</td>
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<tr>
<td>Sampling day 2</td>
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<td>7.3</td>
<td>12.6</td>
<td>1.7</td>
<td>0.6</td>
<td>0.2</td>
<td>0</td>
<td>0.4</td>
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<tr>
<td>Sampling day 3</td>
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<td>8.0</td>
<td>12.1</td>
<td>1.6</td>
<td>0.6</td>
<td>0.1</td>
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<td>0.3</td>
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<tr>
<td>Sampling day 3 (test 1)</td>
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<td>78.7</td>
<td>7.9</td>
<td>12.1</td>
<td>1.6</td>
<td>0.6</td>
<td>0.1</td>
<td>0</td>
<td>0.4</td>
<td>0.9</td>
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<tr>
<td>Sampling day 4 (test 2)</td>
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<td>63.2</td>
<td>7.5</td>
<td>12.5</td>
<td>1.4</td>
<td>0.6</td>
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<td>0.8</td>
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<tr>
<td>Sampling day 5</td>
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<td>0.9</td>
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<td>Sampling day 6</td>
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<td>7.4</td>
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The cement industry has long been dependent on the use of fossil fuels, although a recent trend in replacing fossil fuels with alternative fuels has arisen. However, when unconverted or partly converted alternative fuels are admitted directly in the rotary kiln inlet, the volatile released from the fuels may react with sulphates present in the hot meal to form SO₃. Here Maria del Mar Cortada Mat and associates describe pilot and industrial scale experiments focusing on the factors that affect SO₃ release in the cement kiln inlet.

**Sulphur release from alternative fuel firing**

- **Sulphur can be introduced to cement rotary kilns by** the cement raw materials and/or by the fuels. Biomass fuels such as wood waste and straw contain between 5-10 times less sulphur than fossil fuels. A large difference in sulphur content between fossil fuels also exists. The gaseous SO₂ coming from burner fuel and thermal decomposition in the rotary kiln flows to the clinker, where good gas-solid mixing and the temperature favours nearly 100% capture of the SO₂ with lime (CaO), forming calcium sulphate (CaSO₄). Calcium sulphate, whether sourced from the raw materials or formed in the clinker, will be incorporated in the hot meal entering the rotary kiln.

Consequences of the combustion of alternative fuels in the rotary kiln can include:

- **Direct physical contact between the fuels and the cement raw materials;**
- **Local restraining conditions in the bed material of the rotary kiln;**
- **Potential increase of internal circulation of sulphur, chlorine and alkali metal species.**

These consequences result in modified process conditions and may affect the clinker quality and the process operation, causing build-ups, blockages and/or corrosion. The formation of build-ups and blockages is a consequence of high internal circulation in the kiln of the volatile elements, which are sulphur, chlorine and alkali metals. This article focuses on the kiln inlet of the rotary kilns and sulphur recirculation.

**Sulphur recirculation**

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The combustion of alternative fuels in direct contact with the bed material in the kiln inlet may result in SO\textsubscript{2} release resulting from the decomposition of CaSO\textsubscript{4}, by reducing gases released by the fuel. The main volatile compounds released from the fuels are CO(g), CH\textsubscript{4}(g) and H\textsubscript{2}(g). Consequently, CaSO\textsubscript{4}(s) decomposes according to reactions 1, 2, and 3, resulting in the release of SO\textsubscript{2}(g). In the calciner, the SO\textsubscript{2} can again be absorbed on the CaO to form CaSO\textsubscript{3}, thus, an internal sulphur cycle is established in the rotary kiln and the calciner, which increases the intensity of the sulphur cycle in the kiln.

Thus, an internal sulphur cycle is established in the rotary kiln and the calciner, where they cause blockages. In severe cases, it may be necessary to shut down the cement plant to remove the deposits.

\textbf{Pilot plant experiments}

Sulphur release from the raw material due to combustion of alternative fuels has been studied on a pilot scale setup that simulates the cement kiln material inlet. Investigations of the effect of fuel particle size and the degree of fuel devolatilisation have been made. The industrial scenarios presented in Figure 1 were used as guides for the experiments where non- or partly converted alternative fuels may fall into the rotary kilns.

\textbf{Equipment}

The experiments were performed in a high temperature rotary drum, which simulates the process conditions at the material inlet end of an industrial rotary kiln (Figure 2). The rotary drum is electrically heated by a furnace. Gas can be introduced into the chamber furnace through a hole in the roof in order to have a controlled atmosphere. An externally placed gas pump transports the gas through the rotating drum and the steel tube, after which the gas exiting the reactor, which includes CO\textsubscript{2}, CO, and O\textsubscript{2}, is cooled and analysed. The chamber furnace door is equipped with a window for visual inspection, two holes for thermocouples and a centrally placed water-cooled tube for the introduction of solid fuels. The solid fuels are placed in a sample container which can be pushed into the hot rotary drum or pulled out to the water cooled tube.

The experiments were performed with a constant flow of 100NL/min of air mixed with N\textsubscript{2} at 900°C. The cement raw materials were based on a synthetic mixture of coarse quartz sand with a particle size ranging from 0.5-0.7mm and 2wt% CaSO\textsubscript{4}. The mixture was placed in the rotary drum in the desired volumetric filling degree of 5%.

\textbf{Fuels}

Pine wood cylinders with diameters of 19, 13, and 8mm were used as fuel. All cylinders had a length of 25mm. The fuel analysis and the lower heating value (LHV) are shown in Table 1. All experiments used the same energy input of 95kcal. This relates the mass of the wood cylinders was kept constant, therefore five cylinders of 8mm diameter, two cylinders of 13mm diameter and one cylinder of 19mm were used. Wood charcoal made from the pine wood cylinders was pyrolised in a horizontal tube reactor under a nitrogen atmosphere for 20min at 300, 500, 700, and 900°C in order to obtain wood char with different degree of volatiles. The degree of devolatilisation was calculated on the basis of the volatile concentration before and after pyrolysis, which is 25% for the wood charcoal at 300°C, 90% for the wood char at 500°C and 100% for the wood char made at 700°C and 900°C.

High levels of SO\textsubscript{2}(g) increase the risk of deposit build-up and corrosion. The deposits typically accumulate in the material inlet end of the rotary kiln or in the riser duct between the calciner and rotary kiln, where they cause blockages. In severe cases, it may be necessary to shut down the cement plant to remove the deposits.
The influence of the pine wood particle size and oxygen content on SO₂ release from the synthetic raw materials at conditions corresponding to the kiln inlet is illustrated in Figure 3. For all particle sizes, SO₂ release decreases with increasing oxygen concentration. The high oxygen concentration in the atmosphere may react with the reducing agent and thereby lower its concentration. Another possibility is that the oxygen may influence the reductive decomposition reactions.

The experiments performed with the wood char at different temperatures showed that only the non-pyrolysed wood and wood char made at 300 and 500°C caused SO₂ release. No SO₂ was measured during the experiments with wood char made at 700 and 900°C. Figure 4 presents the total SO₂ release from the raw materials as a function of the particle size of the combusted non-pyrolysed wood and wood char made at 300 and 500°C. The results show that the SO₂ release decreases with decreasing degree of devolatilisation.

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Additionally, the char combustion step for the wood char does not provoke SO₂ release. This is contradictory to the general experience when unburned petcoke is admitted to the kiln inlet causing a dramatic increase in sulphur circulation.·

It was also observed that SO₂ release increases with decreasing particle size. For example, the SO₂ concentration peak reached higher values for the 8mm pine wood particles than for the larger particle dimensions under the same conditions (Figure 5). This is because the smallest particles are heated faster and release the volatile gases faster and in higher concentrations. Consequently, stronger local reducing conditions are formed. The total SO₂ release increases, as previously discussed, with decreasing particle size of non-pyrolysed wood and wood char made at 300°C. There is a big difference in the SO₂ release for wood char made at 300 and 500°C due to the degree of devolatilisation, 90%, whereby few volatile gases are released.

Industrial investigation of SO₂ release

Industrial scale measurements that investigate the relationship between organic carbon in the bottom stage cyclone and SO₂ in the kiln inlet were conducted. Organic carbon from the fast material is balanced to be directly related to unburned calciner fuel. Unburned fuel particles may be carried upwards with the gas flow through the calciner and transported into the bottom stage cyclone. The char particles may therefore arrive in the kiln inlet and their subsequent combustion may cause the release of SO₂.

The investigation was carried out at a cement plant with two separate line calciners. The strings, named A and B, are identical and consistent with a calciner and three cyclones (Figure 6). The raw materials are wet and form a slurry that is introduced into the dryer crusher where it is dried and ground. The dry raw materials are then carried upwards to the top cyclone by a gas stream. The gases in the preheater tower are bypassed from the second cyclone to the dryer crusher before going to the top cyclone, which works as a gas/air separator. The hot air from the calciner cooler goes to the calciner and the rotary kiln gases are mixed with the calciner outlet gases.

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The fuels used in the calciners are petcoke, plastic, and paper-based refined diesel fuel (RDF). Sometimes tyre chips are fired in the riser duct from 2m above the kiln inlet. The fuel analyses of petcoke, RDF and tyre chips are specified in Table 2.

The cement plant controlled the calciner temperature by adjusting the flow of petcoke. In order to estimate the amount of RDF fired, the percentage of fuel input to each calciner originating from petcoke is calculated in Equation 2. The percentage remaining in the calciner after firing corresponds to RDF.

Two tests were performed at the plant:

- **Test 1**: Increase of RDF firing in calciner A (from 37 to 85% RDF of calciner fuel input, while petcoke flow was decreased from 4t/hr to 1t/hr). No tyre chips were fired.

- **Test 2**: Increase tyre chips injection in the kiln inlet from 0 to 2.5t/hr.

Hot meal samples were taken from the bottom cy-clone of strings A and B during eight sampling days over a one month period. The hot meal samples were taken with an FIMCS sampler to assure homogeneous density and to avoid contamination of the carbon. The O₂, CO₂ and SO₂ concentrations in the kiln inlet, CO and O₂ out of the preheater, the petcoke and tyre chips flows and the calciner temperatures were recorded (Table 3). The SO₂ gas measurement in the kiln inlet always recorded a few ppm of SO₂ during the sampling period (Table 3). Therefore, the organic carbon combustion was similar to the petcoke and the organic carbon content in the hot meal samples cannot be related to the SO₂ in the kiln inlet. However, it may be possible that the content of organic carbon measured in the hot meal under such conditions provokes minor SO₂ release, that the analyzer was unable to detect.

The organic carbon from the hot meal samples correlates to the percentage of fuel input to each calciner coming from the petcoke (Figure 7). The results show that the levels of organic carbon increased when the petcoke content was increased and the RDF content was reduced. As such, it may be concluded that the organic carbon in the unconverted carbon comes from the petcoke, since it has a higher concentration of fixed carbon than RDF. According to Figure 7, it would be advantageous to fire higher content of RDF; however, the cement plant found that firing large amounts of RDF caused pressure control problems. The volatility of the SO₂ in the kiln inlet was as- sociated with the sulphur evaporation factor εSO₂ (Equation 3). The dust circulation from the coolers and the kiln to the bottom stage cyclone was disregarded. The clinker was measured every second hour. It was assumed that the dinker analysis corresponds to the hot meal sample after 30min from the time of sampling, which correlates approximately to the residence time of the solid material in the rotary kiln. Figure 9 shows in more detail the function of the organic carbon of the hot meal samples. There is no clear relationship between organic carbon and SO₂ content in the kiln inlet. This supports the observation in the wood char experiments where the SO₂ volatility was not affected by char combustion.

**Conclusions**

The combination of alternative fuels in direct contact with the kiln bed increases sulphur recirculation when they are fired directly into the kiln inlet or when they end up in the kiln inlet because they have not reached full conversion in the calciner. The experimental work shows that SO₂ release from the raw materials takes place primarily during devolatilization and not during char combustion when firing biomass as an alternative fuel. The industrial-scale observations did not show any correlation between εSO₂ and the organic carbon content in the hot meal samples, the fraction of the calciner fuel fired as RDF, or tyre chips firing in the kiln inlet.
The pilot plant experiments indicate that SO$_2$ release decreases with increasing oxygen concentration. Smaller particles in the kiln charge increase SO$_2$ release because they are heated faster and thus release the volatile gases faster and in higher concentrations. However, when admitted to the calciner, fine RDF particles will generally burn in suspension, thereby never reaching the kiln charge, whereas larger particles will. When firing fuel directly into the back end of the kiln the experimental results explain why it may be more advantageous to use coarse chips or whole tyres rather than finer particles.

References

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